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# HYDROCARBON PROCESSING<sup>®</sup>

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**Cover Image:** Clariant's flagship commercial sunliquid® cellulosic ethanol plant in Romania. Photo courtesy of Clariant.



## Calling for papers on the global hydrogen sector

In January 2021, Gulf Energy Information—publisher of *Hydrocarbon Processing* and *Gas Processing & LNG*—launched *H2Tech*. This technical publication focuses on the latest technologies, trends, capital investments and know-how that are shaping the global hydrogen market. *H2Tech* focuses on hydrogen technology across all spectrums—from green (via renewable energy) to blue (via natural gas) to all other forms (brown, black, turquoise, etc.).

The creation of *H2Tech* was inspired by the increasing prominence of hydrogen's usage in advancing the energy transition and leading decarbonization efforts around the globe. The refining and petrochemical industries are no stranger to the production and use of hydrogen within plant operations. It is a crucial part of the processing puzzle to create products in great demand around the world.

**Topics and authorship.** Since the processing industries are aware and focused on the use of hydrogen in many applications, as well as its benefits in the global energy transition, the editors invite our readers to supply the latest technologies affecting the global hydrogen market. *H2Tech* is currently looking for exceptional technical articles/columns that focus on the latest advancements in the hydrogen sector.

The hydrogen industry is not solely within the processing industries, so *H2Tech* has branched out to several different value chains where the use of hydrogen can make a difference in reaching net-zero goals. Examples include transportation/mobility (e.g., aviation, automotive, mass transit, heavy-duty shipping, marine), power systems, green ammonia/methanol production, infrastructure/transmission (pipelines) and more.

The following is a list of topics featured within the publication:

- Blue/green hydrogen production
- Capital project investments
- Chemical/fertilizer production
- Digital technologies
- Electrolyzer technology
- Environmental/regulatory trends
- Fuel cell applications
- Hydrogen storage
- Marine applications
- Measurement/instrumentation
- Mobility applications
- Process/plant optimization
- Regional outlooks/analysis
- Safety and sustainability
- Turbomachinery and compression.

For a full list of topics, contact [Editors@H2-Tech.com](mailto:Editors@H2-Tech.com).

If you are interested in submitting a technical article/column, trends analysis report, executive viewpoint, etc., for *H2Tech*, contact Lee Nichols at [Lee.Nichols@HydrocarbonProcessing.com](mailto:Lee.Nichols@HydrocarbonProcessing.com). The editors of *H2Tech* are eager to work with you on the latest advancements affecting the global hydrogen market. **HP**

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## Pathways towards a more sustainable HPI

Among the dominant, far-reaching themes within the global refining and petrochemicals industries are the increase in biofeedstocks processing to produce biofuels and greener petrochemicals, the continued push towards clean fuels production, regulations and initiatives to adhere to net-zero emissions targets, and a surge in capital investments to build renewables and sustainable aviation fuels (SAF) plants.

These sustainability issues are collectively steering the global hydrocarbon processing industry (HPI) further along in its energy transition. New processes, technologies and digital tools adoption are enabling producers to mitigate carbon emissions during processing, optimize production, increase energy efficiency and produce sustainable products that the world demands.

To accomplish these goals, technology licensors around the world are investing in new research and development initiatives to find pathways for greener and cleaner production processes. These actions are enabling the HPI to advance steadily through the energy transition and provide solutions to enhancing production in a more sustainable way.

In turn, refining and petrochemical producers are investing heavily in new biofuels capacity, SAF production plants, carbon capture and storage initiatives, and circular economy technologies. Many countries around the world are witnessing the establishment of new “green” capacity, whereby plants are utilizing hydrogen to produce green ammonia and methanol or re-routing unused gas back into the production process. Advanced biofuels are being produced through multiple processing techniques and new processes are being adopted to decarbonize the skies.

**Special focus.** Because new processing technologies are vital to the HPI, especially in clean fuels, biofuels and green petrochemicals production, *Hydrocarbon Processing* has increased its coverage of these

topics for several years. This year, these types of sustainable topics have been included within every issue of the technical publication. These range from new refining and petrochemical processes, CO<sub>2</sub> mitigation and carbon capture technologies to plastics recycling, effective circular economy initiatives, bio-based petrochemicals production and new ways to increase environmental prowess in plant operations.

This focus has led to this month's special focus on biofuels, alternative fuels and green petrochemicals. These technical articles, columns and viewpoints showcase the operational and technical know-how to optimize HPI production towards a cleaner and sustainable industry. They will help plant personnel better understand the many pathways available to enhance operations, increase energy efficiency and mitigate emissions.

Several of these topics/themes center on the following aspects of sustainable operations:

- How Dow Chemical's Terneuzen (Netherlands) plant utilized mechanical vapor recompression as a more energy-efficient and sustainable energy supply
- The use of recycled CO<sub>2</sub> as a feedstock for additional petrochemicals production
- A detailed analysis on the results of processing blends of soybean oil and straight-run gasoil and 100% vegetable oil for renewable diesel production
- The beginning of a two-part series covering seven pathways to decarbonizing the oil and gas and petrochemical industries
- A study on increasing blending of bio-oxygenates in gasoline to increase profits.

These technical articles are just a few of the many ways the HPI is evolving towards more sustainable operations and production of the products demanded globally. **HP**

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Pierroberto Folgiero, Chief Executive Officer, Maire Tecnimont, provides his insights and views on how technology will be the key asset in the second wave of the circular economy.

#### 20 Special Focus.

This month's Special Focus details the latest technologies, processes and know-how to better produce biofuels, increase renewable fuels production and provide a more sustainable energy source to produce petrochemicals.

#### 63 Catalysts.

Hydroprocessing catalysts are an essential part of any refinery involved in the treatment/conversion of most petroleum fractions ranging from naphtha to residue. Thailand's PTT Global Chemical discusses pitfalls in planning and selecting the catalyst evaluation method and provides best practices to guide refiners towards optimal hydroprocessing catalyst selection.

#### 66 History of the HPI.

This month's history section provides notable technological discoveries of the 1960s, and the people that were instrumental in advancing the global refining and petrochemicals industries.

#### 79 Engineering and Construction.

New management methods are needed to curb the frequent delays and cost overruns in capital projects. The root cause of these problems is the difficulty in managing the inherent complexities of large engineering and construction projects. This article highlights the deficiencies of today's working practices and proposes a practical method to manage complexity.



## Insights from the 2020 Worldwide Fuels Refinery Performance Analysis

The author's company recently completed its data analysis for the 2020 *Worldwide Fuels Refinery Performance Analysis (Fuels Study)*. With its inception in 1981, this biennial survey—representing up to 85% of the worldwide refining capacity—generates a rich and unique collection of operating data and insight. Of particular interest is the impact that COVID-19 has had on the worldwide refining industry. This article shares general insights and observations on the 2020 pandemic impacts and decisions that will potentially shape the future of refining.

**Utilization.** Worldwide utilization was down approximately 10% in 2020 as refiners adjusted run rates to match lower transportation fuels demand; however, Europe fared better than other regions around the world in terms of overall utilization (FIG. 1). It is interesting to note that utilization impacts from the pandemic were more severe than the 2008 financial crisis, as indicated by the greater destruction of transportation fuel demand.

**Profitability.** Net cash margin was impacted by both crude pipeline availability and transportation fuel demand destruction. While all regions around the world had lower profitability in 2020 vs. 2018, refiners in the Eastern Hemisphere were particularly impacted. FIG. 2 shows the hardest hit regions were Russia, followed by Western Europe, the Middle East and Asia-Pacific. In the U.S., inland refiners saw their crude cost advantage erode as pipeline capacity became available due to lower refinery utilization.

**Capital expenditures.** Worldwide capital investment was 16% lower in 2020 vs. 2019 as refiners attempted to bolster cash flow. At 35%, the U.S. and Canada

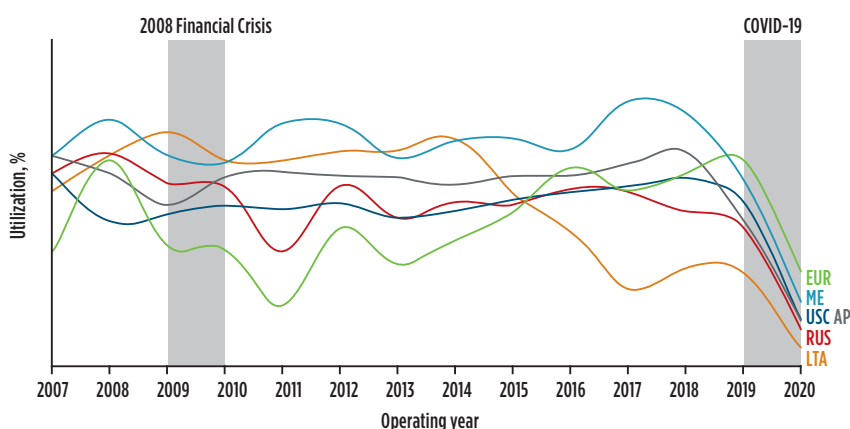


FIG. 1. Refining utilization rates by region.

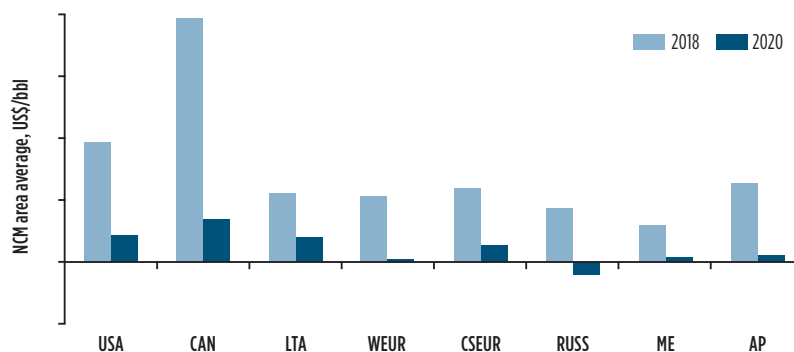


FIG. 2. Regional net cash margin changes.

experienced the largest reduction vs. other regions. The lagging effect from this reduction in capital investment is a reduction in demand for the construction industry, which must be able to restart quickly and deal with supply chain issues as refiners begin spending capital as margin outlooks improve.

In the future, 25% of the *Fuels Study* participants plan to increase their capital spending by 50%, mainly in energy conservation. The author's company believes these refiners appreciate that being more

energy efficient will not only reduce carbon emissions but also positively impact maintenance and personnel costs.

**Operations staffing.** More than half of the study participants maintained normal shift and relief schedules. To minimize personnel exposure, mitigation measures included the following:

- Restricted access to control rooms
- Minimizing extra operators on shifts
- Isolating central control.

Many operators retrained/qualified members of the non-operations workforce for backup contingency to work processing units in case an insufficient number of operators were unavailable due to COVID-19. Ten percent of the participants needed to use non-operations personnel to alternately staff units. Some changed their shift schedules (moving from a 12-hr to an 8-hr shift) to allow childcare flexibility since many schools closed and went to online formats. Several participants implemented technology to allow electronic communication between operators in the field and support staff to minimize face-to-face interactions.

In the future, one-third of participants plan to improve the level of field automation to reduce the minimum operating staff needed for safe operations. While automation cannot totally replace human operators, it can eliminate recurring tasks performed by operators on processing units, allowing the remaining staff to focus on safe, environmentally compliant, reliable and profitable operations.

**Maintenance staffing.** More than half of the study participants changed maintenance schedules, driven by the need to reduce exposure and perform critical activities only. Adjustments included the following:

- Staggering report times
- Putting technicians on shifts
- Scheduling cohorts 7 d on/off
- Switching between a 3 d on/4 d off and 4 d on/3 d off work week.

Two-thirds of participants reduced their contractor staffing levels due to a reduction in base maintenance activities and lack of contractor availability. Staff-

ing schedules were adjusted to mirror company maintenance resources. Contractor costs increased due to disinfection, idle/waiting times and increased personal protective equipment.

In the future, nearly half of the study participants plan to reduce their reliance on non-turnaround maintenance contractors, primarily driven by setting specific limits for cost reduction. Some respondents plan to use nested non-turnaround contractors during turnarounds.

**Non-field personnel.** Nearly all study participants allowed their non-field personnel and support staffs to work remotely from home or work alternative schedules. Only 10% are re-evaluating consolidating their general and administrative personnel, outsourcing to fewer countries. Many are increasing their information technology resources to support online communications.

**Health and safety.** Nearly all study participants plan to update their response measures for future pandemics as dictated by their local/national governments. Risk mitigation examples include:

- Requiring contractors to submit their own pandemic response plans
- Allowing employees to self-screen temperature checks at site entrances
- Using temporary buildings and structures to enable social distancing
- Wearing masks indoors
- Staggering lunch times
- Enacting mandatory quarantine and COVID testing upon return from travel to high-risk regions.

**Maintenance turnarounds.** The pandemic forced refiners to rethink their traditional maintenance turnaround strategy. Refiners could have enacted any of the following strategies:

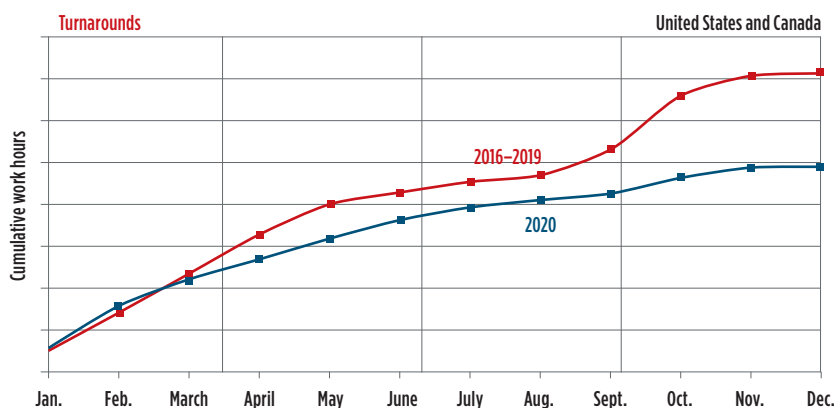
1. Defer shutting down units for maintenance due to negative cash margins, worker health concerns and equipment delivery delays.
2. Shutdown units for turnaround due to a pressing need to address mechanical integrity and process safety concerns.
3. Potentially take a longer time to execute turnarounds to manage worker health concerns and negative cash margins.

Most turnarounds are scheduled to occur at intervals of 4 yr–6 yr between downtimes. The author's company compared cumulative turnaround work hours to averages witnessed in 2015–2016. Most regions had a decrease in total turnaround work hours except for the Middle East and Central/Southern Europe.

**FIG. 3.** focuses on turnaround work hour patterns in the U.S. and Canada. Cumulative work hours in 2020 trended in line with previous averages for 1Q 2020. Work hours plateaued in 2Q 2020 when COVID lockdowns were enacted around the March timeframe. However, we did not see the normal increase in fall season work hours after the high gasoline demand for the summer driving season was over.

This data suggests that more refiners chose turnaround deferral. However, what are the longer-term impacts of this strategy? Would postponing turnarounds lead to more equipment breakdowns and unit downtimes as refiners attempt to stretch intervals another 1 yr–2 yr? Would these unplanned events happen during times of higher margins, leading to higher lost opportunity for increased profitability?

Operational availability is the author's company's metric for measuring when a unit is available to run regardless of economic conditions. **FIG. 4** shows historical operational availability from 2010–2020. This data shows a mixed result for each region. Many regions with lower operational availability had more unplanned downtimes. Were these unplanned downtimes caused by lower availability of maintenance personnel and resources due to the pandemic? Some regions ex-



**FIG. 3.** U.S. and Canada turnaround work hours.

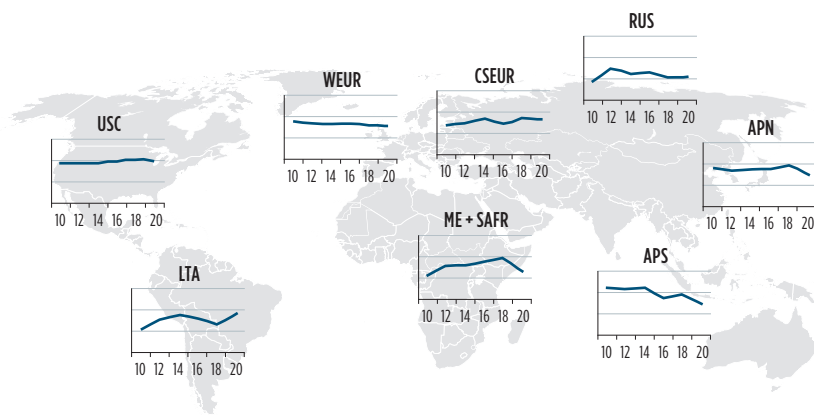


FIG. 4. Regional operational availability, 2010–2020.

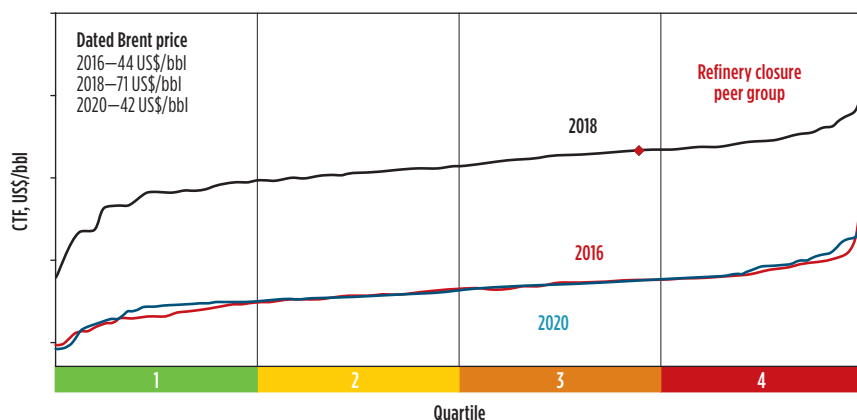


FIG. 5. Worldwide CTF with refinery closure peer group.

performed lower unplanned downtimes. Was this because running at lower utilization put less stress on the equipment?

This variability indicates the need for additional data. The 2022 *Fuels Study* will collect operational and turnaround data for both 2021 and 2022, shedding light on which turnaround strategy was the best option (i.e., should refiners have deferred their turnarounds or not).

**Potential refinery closures.** The author's company's cost of transportation fuels (CTF) metric gauges a refinery's survivability. CTF is the breakeven price for a refiner to produce a barrel of transportation fuel. This breakeven price includes net raw material cost and operating expense. A refinery's location may have an impact on CTF for access and logistics to deliver cheaper raw materials. Regions with higher energy prices also drive refiners to lower their non-energy costs to remain competitive. Refineries with a higher CTF are at risk of going out

of business. FIG. 5 shows the worldwide CTF distribution, including a refinery closure peer group showing the average CTF position for refineries in the study that announced either closure or conversion to renewables production.

Refineries operating on the left side of the curve (a lower CTF) can go on the offensive, using their lower breakeven cost plus advantaged freight rates to transport products. Refineries with a higher CTF in those markets must go on the defensive to remain profitable. Refineries operating in the range of the closure peer group are at risk for closure, conversion or divestment to another buyer. Demand destruction may be the accelerator for additional refinery capacity going offline. The author's company's proprietary database model<sup>a</sup> evaluates regional product demand and trade flows to calculate at-risk capacity to return regional utilization to 80% as product demand decreases. Under a 2°C temperature increase scenario case, the

author's company estimates that 15%–20% of global refinery capacity is at risk by 2030, with an additional 20% of capacity at risk by 2040.

**Sustainability.** Net-zero emissions goals will continue to transform the refining industry. The author's company's proprietary metric<sup>b</sup> accounts for most of a refinery's Scope 1 and Scope 2 greenhouse gas (GHG) emissions. The metric has a direct link to refinery energy efficiency. As refiners ramp up run rates, increased utilization from better reliability will improve energy efficiency. When formulating a sustainability strategy, refiners should agree on a percentage reduction for GHG emissions in carbon dioxide equivalent (CO<sub>2</sub>e), which can translate to a concrete energy efficiency goal. If strategic investments are required to meet this goal, an acceptable rate of return can be generated using process constraint removal and non-energy operating expense reduction credits.

**Takeaway.** The pandemic has had significant impacts on utilization, profitability and cash flow for the refining industry, and has forced refiners to rethink how to staff and maintain their facilities in a demand destruction environment. The resulting demand destruction and sustainability initiatives point to additional rationalization of refining capacity in the next several years. Participation in the 2020 *Fuels Study* allows participants to shape their future strategies to deal with lower (and already declining) transportation fuels demand, which the pandemic has likely hastened. **HP**

#### NOTES

<sup>a</sup> Solomon's World Oil Refining Logistics and Demand (WORLD<sup>2</sup>) Model

<sup>b</sup> Solomon's Carbon Emissions Index (CEI™)



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## Consider packaged twin-screw compressors

Compressors are widely used in the process industries to move fluids and gases within and outside the boundary of a process. The fluids can be any compressible fluid—either gas or vapor—and can have a wide range of molecular weights. The compression of gases and vapors is an important operation in the chemical and petrochemical industries.

Depending on the application, these machines are constructed and configured in various ways. They can be divided into two primary groups: intermittent and continuous. The intermittent mode of compression is cyclical in nature, in that a specific quantity of gas is ingested by the compressor, acted upon and discharged before the cycle is repeated. Compressors operating in an intermittent compression mode are referred to as positive displacement compressors; the two distinct types within this category are reciprocating and rotary. Reciprocating and rotary screw compressors are intermittent machines.

The continuous compression mode is one in which the gas is continuously being ingested and discharged without flow interruption at any point in the process. With very few exceptions, compressors operating in a continuous mode are referred to as dynamic compressors; the two distinct types within this category are centrifugal and axial.

In process applications of rotary screw compressors, the user-purchaser will find gases that vary from consumer products, such as the home refrigerator, to large complex petrochemical plant installations. Recorded molecular weights of compressed gases cover the range from 2 (hydrogen) to 352 (uranium-hexafluoride).

**Fields of application overlap.** The overlap between the different types of compressors is shown in FIG. 1. During selection, the choice is usually based on economic considerations. However, a combination of initial cost, advanta-

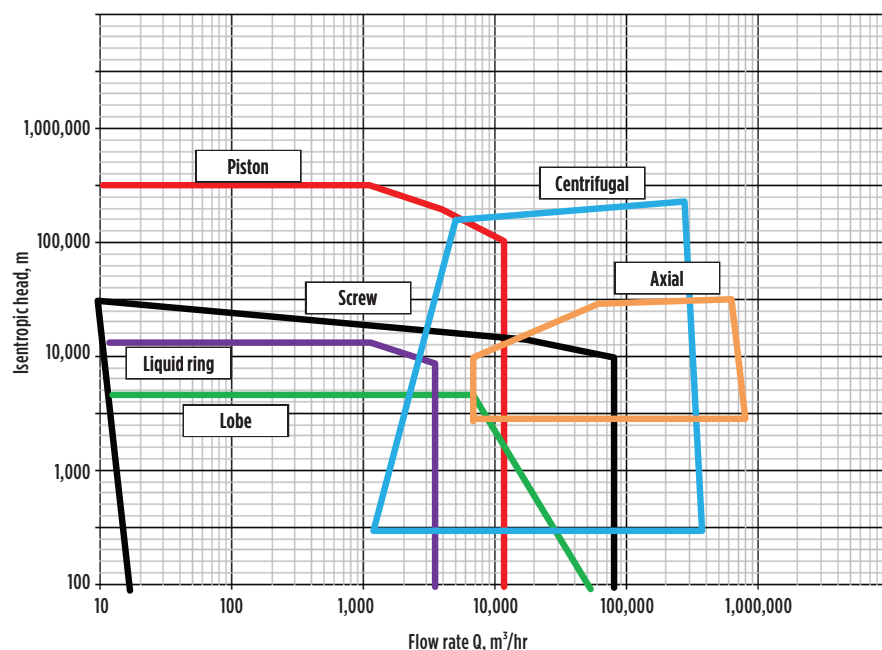


FIG. 1. Selection chart for different types of industrial compressors.<sup>1</sup>

geous efficiencies of carefully engineered asymmetrical rotor contours and projected long-term reliability is indicative of trends that will move today's packaged twin-screw compressors into much closer focus than a few years ago.

Experienced manufacturers of rotary screw compressors offer compressor packages like the one shown in FIG. 2, which depicts a two-stage, oil-free compressor with intercooling. An oil refinery in the UK uses this machine to compress 2,300 m<sup>3</sup>/hr of flare gas from 1 bar to a discharge pressure of 10.1 bar. Interestingly, each stage is equipped with double, self-acting dry gas seals.

What comes to mind are the lessons one could learn from discussing details with this manufacturer. The fact that flare gas is not usually very clean would be a sub-topic in such conversations. Dry gas seals in this machine are a recent choice for such services. However, what prompted this choice? Chances are that

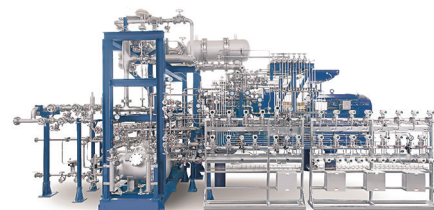


FIG. 2. Fully preassembled two-stage twin-screw flare gas recovery package. Photo courtesy of Aerzener Maschinenfabrik.

the owner-purchaser in the UK received bids or offers for less expensive machines but opted for the one with the best available technology. Exploring the details would be a value proposition.

**Oil-free vs. liquid-flooded twin-screw compressors.** Rotary screw compressors are available in oil-free or oil-flooded construction. Oil-free refers to not having oil in the compression



space, but bearings still require lubrication by a clean medium. This lubricant is typically a clean premium grade lubricating oil, although clean pressurized water, glycerin and several other fluids can also be used.<sup>1</sup> While pressurized water represents less well-known advanced technology, it has been applied for decades. In the hands of truly competent compressor manufacturers, water-flooded screw compressors have been remarkably effective and successful in some of the dirtiest services.<sup>1</sup>

While oil-free twin-screw compressors are widely called “dry-screw” machines, at least one prominent manufacturer defines and designates as dry screw any screw compressor equipped with timing gears. Therefore, whether the compression space is dry, oil-flooded or water-injected makes no difference: With timing gears keeping the two screws synchronized, it should be labeled a dry-screw machine. Without timing gears, it cannot function as a dry-screw machine because the resulting contact of mating rotors would destroy it. If there are no

timing gears, a separating liquid must be used. Any separating liquid introduced to or circulating in the compression space will make it a wet-screw machine.

Wet-screw compressors with single-oil circuits are not suited for heavily contaminated gas streams; such streams have sometimes managed to ruin single circuit machines within days. In one such case, the problem was related to the use of oil filters (25 micron nominal) that plugged after just a few hours of operation. At another installation, asphaltene-contaminated vapors had been allowed to “bubble through” crude oil in gathering tanks before reaching the bearings in several screw compressors.

Fields of application for oil-free machines include all processes that cannot tolerate contamination of the compressed gas or where the lubricating oil would be contaminated by the gas. Oil-flooded machines can achieve slightly higher efficiencies than dry-screw machines and can utilize the oil for cooling, as well. The same statements could be made for water-flooded machines. In

some instances, the bearing lube circuit must be totally separate from the fluid circuit used in the compression space. Whenever this requirement is disregarded, the purchaser-user may end up with either high maintenance costs or low equipment reliability. **HP**

#### REFERENCES

- <sup>1</sup> Bloch, H. and H. Elliott, *Compressor Technology Advances: Beyond 2020*, DeGruyter, Berlin, Germany, 2021.



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# Innovative recycling, driving circularity while decarbonizing the petrochemical industry

Plastic pollution's environmental challenges, as well as new government legislation, are having a significant impact on the plastics industry. Polymer manufacturers are being urged to experiment and implement alternative production processes—such as bio-based plastics and recycling—to decarbonize their products.

The complexity associated with the development of alternative production processes is amplified by the fact that there are a variety of polymers, and the formulations generated by adding additives differ depending on how they are used.

Let us first focus on recycling thermoplastics. Thermoplastic waste can be either mechanically or chemically recycled. Presently, chemical recycling only accounts for about 1% of recycled plastics. However, that proportion is expected to rise sharply, especially given that this approach enables the production of polymers that can be reused in a true circular closed loop, even for the most demanding applications, such as food or pharmaceutical plastic grades.

This field of chemically recycling plastics is where the authors' company has applied its long-standing expertise [chemicals and chemical engineering, catalysis (homogeneous and heterogeneous), analysis, process engineering and modeling, pilot and demonstration design, and scaleup to industrial units] to develop innovative process technologies.

Chemical recycling opens new opportunities to bridge the gap between the need for additional plastics recycling capacity and the need for high-quality recycled plastics products. For example, chemical recycling addresses more difficult waste plastics feedstock that cannot be valorized through mechanical recycling, while fully meeting quality requirements and regulatory objectives. Chemical recycling prevents routing all plastics waste to a mechanical recycling process. It also enables the following:

- Valorizes mixed plastics streams in a closed-loop complex, where sorting and separation stages, and regeneration processes required for recycling are too complex.
- Valorizes plastic polluted during the various stages of its life (from its manufacturing to its arrival at the recycling plant), including contamination from the different sorting steps or contamination from contact with other materials during its use.
- Removes all intentionally added contaminants to allow for a true closed recycling loop of plastic wastes (e.g., pigments, dyes, forbidden additives).
- Creates an infinite closed recycling loop of plastics vs. mechanical recycling, where recycling may be limited

to a certain number of cycles. Those cycles' limitations are due to the temperature effects associated with the various stages of the recycling process, ultimately causing degradation of the recycled raw material and preventing upcycling (e.g., recycling of waste textile into food grade packaging such as bottles).

Chemical recycling (also referred to as advanced recycling) encompasses different processing technologies. Depolymerization and conversion processes can be used to modify the chemical structure of the polymer and purify the resulting product to enable the production of new raw polymers. Dissolution processes are also being developed to recover additive-free polymer chains. Some argue that dissolution is an extension of mechanical recycling, as the chemical structure of the polymer remains unchanged. However, that process relies heavily on chemical stages and is often grouped with chemical recycling.

Depending on the type of polymer waste, some chemical recycling routes are more appropriate than others. For example, waste polyethylene terephthalate that cannot be mechanically recycled will be recycled through a depolymerization process and is not suitable to conversion or dissolution processes.

**The already proven and robust pyrolysis pathway.** The following will focus on the conversion process, with a special focus on mixed plastic pyrolysis and its associated purification and decontamination steps. This is a key building block to a sustainable polyolefin chemical recycling value chain.

Pyrolysis of mixed plastic waste is considered the novel route to accomplish a true closed-loop recycling process of polyolefins, adhering to quality requirements and regulatory objectives. However, this route relies on the ability to properly purify the pyrolysis oil for reprocessing it in an existing petrochemical plant. That purification step is not a trivial refining process, as pyrolysis oil usually combines multiple contaminants and unstable molecules that—if not removed and stabilized—would jeopardize the operation of a petrochemical plant's steam cracker.

Repsol and the authors' company have joined their efforts to unlock the recovery of plastic waste that would otherwise remain in landfills or be incinerated. The consortium has developed and commercialized a proprietary pyrolysis purification process<sup>a</sup> to solve the challenges of purification and decontamination of pyrolysis oils. This process technology removes impurities such as silicon, chlorine, diolefins and other metals from the produced plastics pyrolysis oils, allowing the direct and undiluted feed to the steam cracker. Proper and reliable

purification is paramount, as contaminants could not only jeopardize the operation of petrochemical steam cracker furnaces, but can also leak and concentrate in downstream units, ultimately ending up in polymers produced.

The successful commercialization of the purification technology would not have been possible without the development of new analysis methods by IFP Energies nouvelles to properly assess the different qualities of pyrolysis oil. Pyrolysis oil products concentrate a large proportion of multiple contaminants, making it difficult to analyze through conventional analysis methods.

As pyrolysis oil qualities vary substantially, the proprietary purification process<sup>a</sup> has a unique flexibility (vs. conventional hydroprocessing refining units) to cope with quality changes, enabling it to continually guarantee production of on-specification products suitable for direct undiluted processing in a naphtha steam cracker. In addition to processing the full range of pyrolysis oil, the proprietary purification process<sup>a</sup> can also embed a cracking option that will convert heavier products back to virgin-equivalent recycled naphtha, maximizing the closed-loop production of circular polymers.

Through its collaboration agreement with Plastic Energy, the authors' company is also able to license patented, industrially proven advanced recycling technology, which uses a thermal anaerobic conversion pyrolysis process<sup>b</sup>.

With thermal anaerobic conversion pyrolysis process<sup>b</sup> and proprietary purification process<sup>a</sup>, which are commercial technologies, the pyrolysis pathway for plastics recycling can play an important role in mitigating the environmental impact of plastic waste. It also unleashes the full potential of converting any polyolefin plastic waste into food-grade quality.

At the onset of plastic recycling projects, the authors' company's experts support project developers on questions related to waste feedstocks characterization, technology performance, costs and potential financing strategies, taking full advantage of the unique expertise the company has built and developed with partners in the field of chemical recycling. **HP**

#### NOTES

<sup>a</sup> Axens' Rewind™ Mix technology

<sup>b</sup> Plastic Energy's thermal anaerobic conversion pyrolysis process



**NICOLAS MENET** earned an engineering degree from Ecole Des Mines de Nantes in France. He is also a functional safety certified engineer and holds Lean and Six Sigma qualifications. Mr. Menet has 20 yr of experience in the energy sector and has focused on performance improvements in assets through innovative processing technologies and digital solutions. He now serves as the Development Manager for two plastics chemical recycling technologies launched by Axens.



**THOMAS MALLET** joined Axens in 2005 as Technology Manager for biodiesel technologies. In 2008, he moved to the Olefins Technology Group and has been involved in various technologies aiming at upgrading light olefins from steam cracking and fluid catalytic cracking such as etherification, heterogeneous oligomerization and Atol (ethanol-to-ethylene). He joined the Technology Development and Innovation Division in 2014, where he managed the coordination of R&D activities related to biofuels and biobased chemical components. In 2020, he joined the new Plastic Recycling Business Development Group to manage R&D activities and develop technological cooperations. Mr. Mallet earned an engineering degree in chemistry from the Institut National des Sciences Appliquées de Rouen in France.

## Maire Tecnimont and the second wave of the circular economy



**PIERROBERTO FOLGIERO** joined Maire Tecnimont in 2010 as the Chief Financial Officer of KT S.p.A, the group's subsidiary, operating as licensor and contractor in the refining sector. In 2013, he was appointed CEO. Mr. Folgiero is also the Managing Director of NextChem, the company of the group operating in green chemistry. Mr. Folgiero earned a degree in economic studies from Luiss Guido Carli University.

The circular economy has already entered the public's consciousness, and consumers are increasingly aware of the urgent need to recycle plastic, with the practice becoming more widespread than ever. We are now in a "second wave" of the circular economy, in which we face two challenges:

1. Increase focus on hard to recycle resources
2. Incorporate the circular economy directly into product and process design.

Technology will be the key asset as we move into the second wave of the circular economy. First, upcycling technologies will be essential to succeed in meeting the world's booming demand for recycled

plastic. Unfortunately, recycled plastics are often poor quality. Pure mechanical recycling degrades the material, whereas the upcycling of plastic waste through chemical additives is necessary to regenerate polymer back to its virgin state. The result is a high-quality material that can be used in manufacturing industrial products. Consequently, chemical recycling technologies will be critical for hard to recycle plastics.

Maire Tecnimont's green chemicals unit NextChem has introduced a proprietary technology called MyReplast that can transform both consumer and industrial plastic waste material into a secondary raw material with physical and chemical characteristics and mechanical properties that allow it to substitute virgin polymers from fossil sources.

Additionally, we are also patenting our chemical recycling technologies to cope with the increasing need to avoid landfilling of hard to manage plastic wastes.

It is equally important to recover the carbon and hydrogen ( $H_2$ ) already sequestered in the non-recyclable plastics and the dry part of the municipal solid waste. Our company is launching several projects in Italy and abroad to produce  $H_2$  from plastic and dry waste. This "circular  $H_2$ " is not green, not blue and not purple, but it is very low carbon. It is a way to break the ice and show society that we do not need to wait until 2050 for the  $H_2$  economy.

The big issue for green  $H_2$  is not technological readiness but the broad availability of renewable electrons already needed to switch off coal-fired power plants. Furthermore, renewable electricity is expected to become the main power source in sectors like heating and transportation, where fossil fuels dominate.

In Europe, there is much debate about which electron color can be produced by nuclear energy. Unlike France, Italy and Germany are taking an opposing

view. There is an overwhelming demand for electrification, which must be met if we want to cope with ambitious climate change targets. We need to produce renewable electrons to switch off power plants, for light mobility and to produce renewable electrons to convert to  $H_2$ . There is, therefore, much competition over the availability of a sufficient amount of renewable energy to enable  $H_2$  to happen.

Limited amounts of green electrons may delay the introduction of green  $H_2$ . This bottleneck of green electrons is already visible in Italy, which must build 70 gigawatts (GW) of renewable energy by 2030 but installs fewer than 1 GW/yr. Overall, waste management and circular economy must be part of the solution.

The second challenge of the second wave is the need for the so-called "eco-design" of products to enable as much reuse and recyclability as possible. This is a significant traversal effort to change the manufacturing paradigm from its fundamentals.

The circular economy will be a new mindset to reconceive all industrial processes that will force companies to think outside the box in terms of collaborating across sectors. The circular economy is about connecting dots. It is about a refinery that manages waste or a power company that embraces ammonia and methanol production from electrons. Everyone must go beyond their comfort zone and collaborate differently. This is a big challenge, and we need to join forces. There is no room for rhetoric.

The inventor of polypropylene was an Italian chemist named Giulio Natta, who won the Nobel Prize in Chemistry in 1963. Maire Tecnimont has inherited some of this chemical engineering DNA. Thanks to this patrimony, the company can be part of a circular economy that creates a new, more responsible way to use and conceive plastic. **HP**

# Overview of decarbonization pathways for the oil and gas and petrochemical industries—Part 1

This two-part article will cover the seven pathways to decarbonizing the oil and gas and petrochemical industries. Part 1 will detail sustainability and discuss decarbonization pathways through green and blue hydrogen ( $H_2$ ); biofuels, renewable fuels and e-fuels; and the circular carbon cycle. Part 2—to be published in the June issue of *Hydrocarbon Processing*—will discuss energy efficiency, new technologies, electrification and carbon capture.

**The need for decarbonization.** Carbon dioxide ( $CO_2$ ) is a greenhouse gas (GHG) that traps heat in the Earth's atmosphere, contributing to global warming. To achieve the goal of limiting global warming to  $1.5^\circ C$  above pre-industrial temperatures, it is necessary to significantly reduce  $CO_2$  emissions. By 2030, the European Union (EU) seeks to reduce the region's  $CO_2$  emissions to 55% below 1990 levels (fit for 55), and, by 2050, to be carbon neutral. The U.S. has set goals of reducing its  $CO_2$  emissions by 2030 to 50% lower than 2005 levels, having carbon-free utility power generation by 2035 and achieving carbon neutrality by 2050. Major integrated oil companies have announced goals to reduce  $CO_2$  emissions by 35%–40% by 2030 and to be carbon neutral by 2050. The task ahead is challenging and will require global commitments from governments and industry, along with the development of new technology. The pathways for decarbonization will be different for various industries. This article will discuss some of the pathways toward decarbonization for the oil and gas and petrochemical industries.

Burning natural gas [methane ( $CH_4$ )] creates a lower heating value

(LHV) of 58 kg  $CO_2$ /1 MMBtu.<sup>3</sup> Every 100 MMBtu/hr (LHV) of  $CH_4$  burned on a fired heater will generate 50,000 tpy of  $CO_2$ . This is a good rule of thumb for evaluating the impact of opportunities to reduce  $CO_2$ .

To reach the goal of carbon neutrality, it is necessary to reduce Scope 1, Scope 2 and Scope 3  $CO_2$  emissions. These emissions are defined as:

- **Scope 1 (direct  $CO_2$  emissions):** These are the direct result of burning fuels like natural gas, offgas and fuel oil for process heating, and for generating steam and power at process units.
- **Scope 2 (indirect  $CO_2$  emissions):** These result from imported energy, like purchased steam from neighboring industries or purchased electric power from the power grid.
- **Scope 3 ( $CO_2$  emissions from the use of product):** This is the  $CO_2$  produced by using the product. For an oil company, this is the  $CO_2$  from car and truck tailpipe emissions. For integrated oil and gas companies, 85% of their  $CO_2$  emissions can be Scope 3.

$CO_2$  has a global warming potential (GWP) of 1, which is a reference standard.  $CH_4$  is also a GHG, and has a GWP of 86 for a 20-yr duration and a GWP of 26 for a 100-yr duration.<sup>3,1</sup> Eliminating 1 t of  $CH_4$  leaks has the heat-trapping-reduction equivalent to eliminating 86 t of  $CO_2$ . It is a much easier task to stop  $CH_4$  leakage than to capture  $CO_2$  from the atmosphere. A key priority is reducing  $CH_4$  leakage from abandoned oil wells, gas wells, pipelines, LNG plants and landfills. At the COP26 UN climate change conference, more than 100 nations signed

a pledge to reduce  $CH_4$  emissions by 30% by 2030 vs. 2020 levels. Nitrous oxide and ozone are the other GHGs. The  $CO_2$  equivalent ( $CO_2e$ ) of a stream is the combined  $CO_2$  impact of all the GHGs in the stream. Reducing  $CH_4$  emissions will have an immediate impact on reducing global  $CO_2e$  because of its high GWP.

## What are the sector sources of $CO_2e$ ?

The U.S. Energy Information Agency (EIA) reported that, in 2020, the U.S. generated 4.6 B metric t of  $CO_2e$  from burning fossil fuels with petroleum (45%), natural gas (36%) and coal (19%) (FIG. 1). In 2020, 65% of  $CO_2$  emissions from fossil fuels came from the transportation (36%) and industrial sectors (29%). Opportunities to reduce the carbon footprints of the transportation and industrial sectors include:

- **Transportation:** Producing and selling less carbon-intensive fuels, as well as using renewable and biofuels, renewable electric power, and green and blue  $H_2$
- **Industrial:** Improving energy efficiency; utilizing new and improved technologies; using electrification with renewable power; using green and blue  $H_2$ ; and incorporating carbon capture, utilization and storage (CCUS) technologies.

In FIG. 1, 32% of  $CO_2e$  emissions in the U.S. were from the generation of commercial power. Additionally, while coal generated 19% of the commercial power, it accounted for 54% of total  $CO_2$  emissions from power generation. There are opportunities to replace fossil-fuel-generated electricity with renewable power like wind, solar and geothermal.<sup>2</sup>



**The seven pathways to reducing carbon footprints.** The seven pathways to reducing carbon footprints include a combination of several methods. The ways to reduce Scope 1 and Scope 2 emissions (direct and indirect CO<sub>2</sub> emissions from fossil fuels) include the following pathways:

- 1. Energy efficiency/stopping CH<sub>4</sub> leaks:** Improving energy efficiency in existing and new facilities, maintaining energy recovery equipment, and stopping routine flaring while minimizing flaring on startup and shutdown
- 2. Technology:** Utilizing new processes and catalysts that will improve yields and reduce energy intensity
- 3. Electrification:** Electrifying process equipment using renewable electric power (i.e., wind, solar, hydroelectric, geothermal, nuclear)
- 4. CCUS:** Providing cost-effective carbon capture with the utilization and storage of captured CO<sub>2</sub>

(adding CCUS to biofueled equipment to achieve negative CO<sub>2</sub> footprints)

**5. Green and blue H<sub>2</sub>:** Producing, using and selling low-carbon H<sub>2</sub>.

The good news is that operating companies and supporting engineering companies in the oil and gas and petrochemical industries already have the technology and assets for onshore and offshore wind, blue and green H<sub>2</sub> generation, and CO<sub>2</sub> sequestration and can convert refinery units to make renewable fuel from biofeedstocks.

**Ways to reduce Scope 3 emissions in the oil and gas industry.** As the world begins to use more renewable energy, the use of fossil fuels will begin to reduce. Oil and gas companies will transition to become energy providers that will sell less petroleum-based fuels and begin to sell fuels with low carbon intensity.

Pathway six reduces carbon footprints for Scope 3 emissions by using biofuels, renewable fuels and e-fuels. These include the following:

- Biofuels and renewable fuels, such as renewable diesel and sustainable aviation fuel (SAF)
- Synthetic e-fuels, like e-gasoline, which are made from green H<sub>2</sub> and captured CO<sub>2</sub>
- Low-carbon LNG using CCS during natural gas treatment and the electrification of LNG refrigeration compressors
- Renewable electricity, such as wind (onshore/offshore) and solar photovoltaic (PV) electricity production
- Green and blue H<sub>2</sub>.

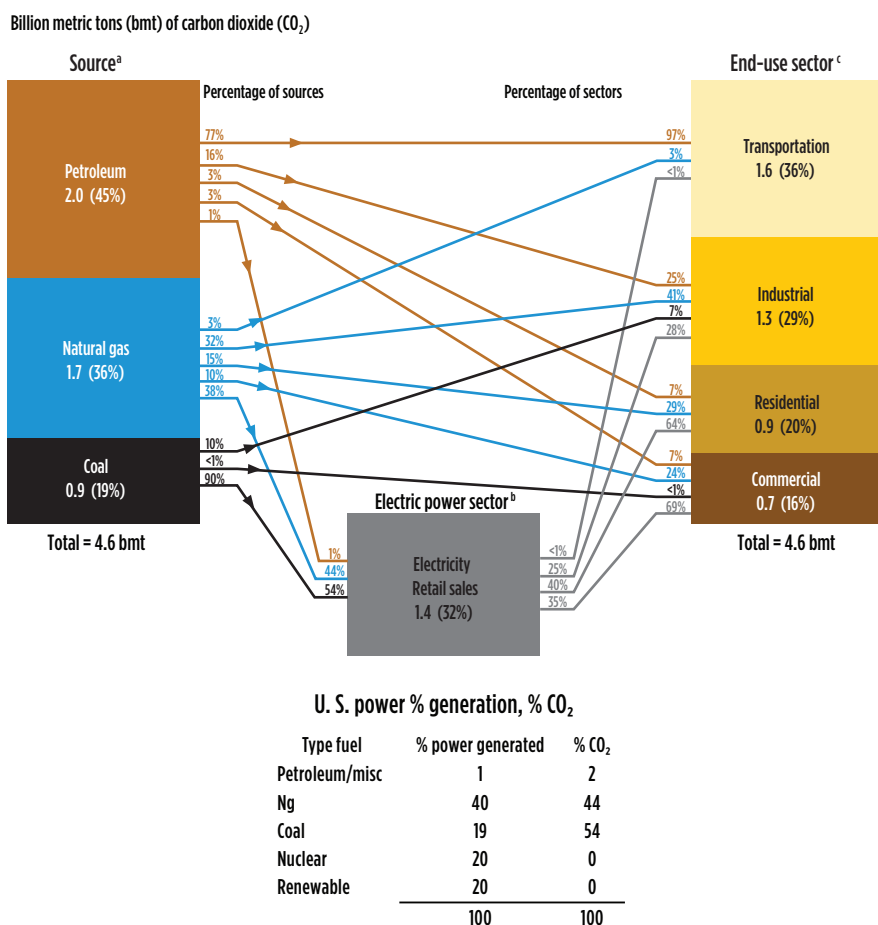
**Ways to reduce Scope 3 emissions for petrochemicals.** The seventh pathway reduces Scope 3 carbon footprints, especially for plastics and chemical production, through a circular carbon pathway, including:

- **Recycling waste plastics:** Creating a circular carbon economy by either mechanical reprocessing or chemical recycling (e.g., pyrolysis, gasification) of waste plastic
- **Use of renewable feedstocks:** Using renewable feedstocks like bio-naphtha to produce the base chemicals ethylene and propylene to decrease carbon intensity
- **Synthetic chemicals production:** These include chemicals like ethanol and methanol produced using renewable H<sub>2</sub> and captured CO<sub>2</sub>.

The following will detail the decarbonization pathways of green and blue H<sub>2</sub>, along with the use of biofuels, renewable fuels and e-fuels. It will also discuss following a circular carbon pathway.

**H<sub>2</sub> as an energy carrier (the role of green and blue H<sub>2</sub> as decarbonization pathways).** H<sub>2</sub>, with its low- or zero-carbon footprint, will play a key role as a fuel—specifically, in the production of renewable fuels, biofuels and e-fuels. It will also enable e-chemistry by the hydrogenation reaction with captured CO<sub>2</sub>. In a decarbonized world, H<sub>2</sub> demand could increase by a factor of 6 times–10 times the current demand. Green, blue and pink H<sub>2</sub> will fill this increased demand.

Most H<sub>2</sub> produced today is gray H<sub>2</sub>, which is made from CH<sub>4</sub> in a steam methane reformer (SMR). Gray H<sub>2</sub> has a high CO<sub>2</sub> footprint and alternate production methods to make blue and green H<sub>2</sub> are



**FIG. 1.** U.S. CO<sub>2</sub> emissions from energy consumption by source and sector, 2020. Source: U.S. EIA.



required. Blue  $H_2$  is also made from  $CH_4$  but has  $CO_2$  capture added on the outlet of the SMR. Green  $H_2$  does not use  $CH_4$  as a feedstock and is made by the electrolysis of water, using renewable energy in an electrolyzer (70% efficiency). Electrolyzers are classified as an alkaline, proton exchange membrane (PEM) and solid-oxide electrolysis cell. A PEM electrolyzer requires 50 MW of electricity to produce 1 t of green  $H_2$ .<sup>3,4</sup> FIG. 2 is a schematic of a PEM electrolyzer, and FIG. 3 is a schematic of a PEM fuel cell. In a PEM electrolyzer, the  $H^+$  ion migrates to the cathode where  $H_2$  is produced and the oxidation of water to oxygen occurs at the anode. In an alkaline electrolyzer, the  $OH^-$  ion migrates to the anode.

The following is a partial listing of  $H_2$  production methods. The carbon intensity ( $kg\ CO_2/kg\ H_2$ ) is shown only as a way of comparing the different methods, and there is a lot of discussion on the absolute values.<sup>5</sup> A partial list of  $H_2$  production methods includes:

- Turquoise  $H_2$ : Electric plasma pyrolysis of  $CH_4$  to  $2\ H_2 + 1\ C$  (uses nuclear power)
- Green  $H_2$ : Electrolysis of water using renewable electricity—low  $CO_2$  footprint ( $0.4\ kg\ CO_2/kg\ H_2$  for wind and  $1.5\ kg\ CO_2/kg\ H_2$  for solar)
- Pink  $H_2$ : Electrolysis of water using nuclear energy for power—no  $CO_2$  footprint ( $0\ kg\ CO_2/kg\ H_2$ )
- Gray  $H_2$ : The use of  $CH_4$  in an SMR with no  $CO_2$  capture ( $9\ kg\ CO_2/kg\ H_2$ )<sup>6</sup>
- Blue  $H_2$ : The use of  $CH_4$  in a reformer with carbon capture
  - $CH_4$  in an SMR with CCS—capturing  $CO_2$  from the reformer outlet ( $4.6\ kg\ CO_2/kg\ H_2$ )<sup>5</sup>
  - $CH_4$  in an autothermal reformer with CCS—capturing  $CO_2$  on outlet of reactors ( $4\ kg\ CO_2/kg\ H_2$ ).

The relative cost to produce  $H_2$  is \$2/kg for gray  $H_2$ , \$3/kg for blue  $H_2$  and \$5/kg for green  $H_2$ .<sup>7,8</sup> The U.S. Department of Energy (DOE) has announced the 1-1-1  $H_2$  Earthshot, which has the goal of producing green  $H_2$  at a cost of \$1/1 kg  $H_2$  within one decade. With improvements in electrolyzer efficiency by 2030, the cost to produce green  $H_2$  will be \$1/kg using green power from the grid at \$20/MWh ( $\$20/MW \times 50\ MW/t$ ). By

2050, it is estimated that 60% of  $H_2$  will be produced by electrolysis and 40% by natural gas in SMRs with CCUS. By 2050,  $H_2$  generation could consume up to 20% of the power generated in the world.<sup>9</sup>

**The many uses of  $H_2$ .** As a fuel,  $H_2$  can be burned directly in fired heaters. It can also be blended up to a 30%  $H_2$  mix with natural gas as a fuel for gas turbines. Technology companies are developing gas turbines that can burn up to 100%  $H_2$ .

$H_2$  can also be blended up to 20% into existing natural gas pipelines without having to change out residential appliances like hot water heaters, furnaces and gas stoves. As the demand for  $H_2$  increases,

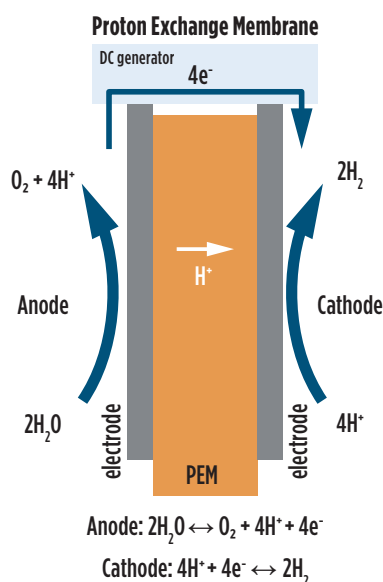


FIG. 2. Schematic of a PEM electrolyzer. Source: IRENA.

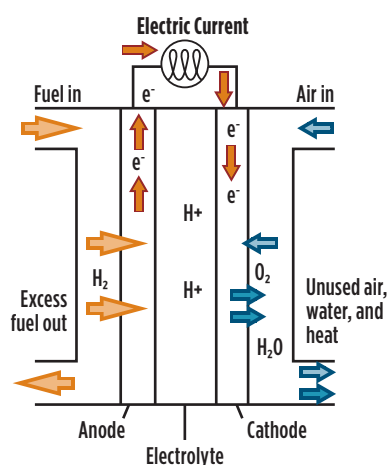


FIG. 3. Schematic of a PEM fuel cell. Source: Wikipedia.

new H<sub>2</sub> pipelines will be built, and some existing natural gas pipelines can be converted to dedicated H<sub>2</sub> pipelines.

Green H<sub>2</sub> should first be used in the chemical and refining processes that require H<sub>2</sub> for hydrotreating and desulfurization, followed by its use in producing synthetic fuels. Replacing gray H<sub>2</sub> with green H<sub>2</sub> will reduce the Scope 3 CO<sub>2</sub> footprints of refining and chemical products. Green H<sub>2</sub> must be used wisely, since it is produced by using renewable power at a 70% conversion efficiency—there is a 30% loss of renewable energy in the electrolyzer.

H<sub>2</sub> is an energy carrier that can be moved by pipelines and trucks. It can also be converted into green ammonia (NH<sub>3</sub>) or green methanol, and then transported by pipelines and ships. Green NH<sub>3</sub> can be converted (dissociation) back into green H<sub>2</sub> at its destination. H<sub>2</sub> can be blended into existing natural gas pipelines and can be extracted from the H<sub>2</sub>/natural gas mix at an endpoint by using pressure swing adsorption and membrane technology. A new technology is liquid organic H<sub>2</sub> carriers, which bond H<sub>2</sub> to organic liquid for transport by pipelines. Since renewable wind and solar power may be generated at remote locations, converting power into H<sub>2</sub> for transport can help reduce future demand on the electric grid. H<sub>2</sub> can also be used as storage for renewable electricity, when grid power demand is low, by converting excess renewable power into H<sub>2</sub> for storage. The H<sub>2</sub> can be used or can be converted back into electric power when needed; however, there is an efficiency loss in the H<sub>2</sub> fuel cell.

An H<sub>2</sub> fuel cell can convert H<sub>2</sub> back into electricity. There are PEM fuel cells and solid-oxide fuel cells. The PEM fuel cell takes H<sub>2</sub>, which is oxidized at the anode, and oxygen (from air) that is reduced at the cathode and generates electricity and water. The reaction in the fuel cell is  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} + \text{electricity}$ . This is the reverse of what an electrolyzer does—i.e., using electric power and water to make H<sub>2</sub> and oxygen. A fuel cell has an efficiency of 60%.<sup>10</sup> Converting electricity to H<sub>2</sub> and then converting H<sub>2</sub> back to electricity has a double efficiency hit, resulting in only 42% ( $0.7 \times 0.6$ ) efficient use of the renewable electric power.

H<sub>2</sub> fuel cell electric vehicles (FCEVs) will have an important role in reducing transportation emissions of electric cars, forklifts, trucks, buses and trains. Many

new forklifts are electrically driven by using H<sub>2</sub> fuel cells. Refueling H<sub>2</sub> vehicles takes half the time of electric vehicle battery recharging. Battery manufacturers are working to reduce charge times. Just as an electrical recharge network along highways is needed, there will also be a need for H<sub>2</sub> refilling stations for vehicles.

Ships can also use green NH<sub>3</sub> as a fuel for long-distance trips—Maersk plans to launch the world's first container vessel operated on green NH<sub>3</sub> in 2023. Green NH<sub>3</sub> is made from green H<sub>2</sub> and green nitrogen by the Haber-Bosch process. The air separation unit providing nitrogen is driven by renewable power. Coal-fired power plants are also planning tests to evaluate burning up to 20%–50% NH<sub>3</sub> as a fuel.

### CO<sub>2</sub> e-chemistry: Power-to-X (P2X).

P2X or CO<sub>2</sub> e-chemistry uses renewable electric power to produce green H<sub>2</sub> and reacts the H<sub>2</sub> with captured CO<sub>2</sub> to make low-carbon gaseous fuels (H<sub>2</sub> and CH<sub>4</sub>), liquid fuels (methanol and synthetic fuels) and chemicals [NH<sub>3</sub> and olefins via the methanol-to-olefins (MTO) reaction]. Using renewable electric power to make H<sub>2</sub> accounts for the “power” or the “e” in the technology name. Green H<sub>2</sub> reacts with captured CO<sub>2</sub> to make syngas, which is a mixture of carbon monoxide (CO) and H<sub>2</sub>. Using Fischer-Tropsch (F-T) chemistry, the syngas can then be converted into organic chemicals and synthetic fuels like methanol, ethanol, e-gasoline, renewable diesel and SAF. The methanol can then be converted to olefins by using MTO technology or into e-gasoline by using methanol-to-gasoline technology. The synthesis reactions to produce methanol from green H<sub>2</sub> and CO<sub>2</sub> are:

- **Step 1 (reforming):**  
 $\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$
- **Step 2 (syngas F-T reaction):**  
 $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$  (methanol)
- **Overall reaction:**  
 $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$ .

Synthetic natural gas (SNG) can be produced by reacting green H<sub>2</sub> and captured CO<sub>2</sub>. The reaction is 80% efficient, so it produces less energy than is put in with the renewable H<sub>2</sub>. The Sabatier reaction is  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4$  (SNG) +  $2\text{H}_2\text{O}$ . This is referred to as carbon circularity. The reaction consumes a lot of H<sub>2</sub>, and a better use of valuable green H<sub>2</sub> is to make synfuels or to use it in chemical and refining operations that require H<sub>2</sub>.

Producing synthetic fuels uses a lot of valuable green H<sub>2</sub> and renewable power. Dry reforming of methane is another route to make syngas from CO<sub>2</sub>. Dry reforming of methane uses CH<sub>4</sub> (not H<sub>2</sub>) to react with captured CO<sub>2</sub> to produce CO and H<sub>2</sub>. The dry reforming reaction is  $1\text{CO}_2 + 1\text{CH}_4 = 2\text{CO} + 2\text{H}_2$ . This reaction does not require green H<sub>2</sub> to convert the CO<sub>2</sub> into CO. The super dry reforming (SDR) process is being developed, which can react 3 moles of CO<sub>2</sub> with 1 mole of CH<sub>4</sub>. The SDR reaction is  $1\text{CH}_4 + 3\text{CO}_2 = 2\text{H}_2\text{O} + 4\text{CO}$ .<sup>11</sup> There is a lot of ongoing research to produce low-carbon synfuels from captured CO<sub>2</sub>. Using gas fermentation, CO can be converted into ethanol; or by using F-T chemistry, syngas is then converted into synthetic fuels.

### Renewable fuels, biofuels and e-fuels: The oil and gas industry's pathway to reduce Scope 3 CO<sub>2</sub> emissions.

For the oil and gas industry to reduce Scope 3 CO<sub>2</sub> emissions, it must transition to becoming energy providers that produce and sell less carbon-intensive fuels like renewable power, green and blue H<sub>2</sub>, renewable fuels, biofuels and synthetic e-fuels. The Low Carbon Fuel Standard (LCFS), created by the California Air Resources Board (CARB) in 2009, provides attractive credits to producers of low-carbon fuels. California's goal is to replace petroleum-based diesel with renewable diesel by 2035.

Demand for petroleum-based gasoline, diesel and jet fuel will decrease. Some energy consultants have predicted that world oil production will peak by 2031 and will gradually decrease by 40%–50% by 2050. Some refineries will shut down or reduce crude throughput and will convert some of their processing units (e.g., hydrocracker and fluid catalytic cracking units) to hydrogenate renewable feedstocks to produce renewable diesel, bio-naphtha and SAF. These low-carbon fuels will be required in addition to the electrification of vehicles (e.g., battery electric vehicles and H<sub>2</sub> FCEVs) to meet the world's growing transportation demand. Renewable feedstocks have a high level of unsaturates and oxygen requiring hydrogenation, resulting in high H<sub>2</sub> demand and high heat generation. Refineries converting to processing renewable feedstocks will need more H<sub>2</sub> and may have to add additional heat removal capacity or operate at reduced rates.<sup>12</sup>

Renewable fuels have a lower carbon intensity than fossil fuels because they are produced from renewable resources. Renewable fuels include biofuels, green  $H_2$  and synthetic fuels. Renewable biofuels are produced from oil seed crops like soybean and canola; from tall oil, corn oil, rapeseed and sugar cane; from lipids like vegetable oils, used cooking oil, animal fats and algae; and from cellulosic material, such as crop residues and wood biomass.<sup>13</sup>

Biofuel feedstock is derived from living matter that removes  $CO_2$  from the atmosphere as it grows. When the feedstock is converted into biofuel and burned,  $CO_2$  is released. This released  $CO_2$  is then removed from the atmosphere when the next crop is replanted (renewed). This  $CO_2$  balance is called the “circular carbon cycle” and can result in close to net-zero  $CO_2$  emissions for biofuels. There is a small  $CO_2$  footprint associated with farming and processing feedstocks that prevents reaching net zero. If the  $CO_2$  generated from burning biofuels is captured by CCUS and the  $CO_2$  does not go back to the atmosphere, then using biofuels can have a negative  $CO_2$  footprint, as  $CO_2$  is being removed from the atmosphere. The use of biofuels with CCUS has a bigger impact on decarbonization.

Renewable diesel meets all the specifications for petroleum-based diesel and is produced by hydrotreating non-petroleum feedstocks, such as waste vegetable oils, animal fats or biomass. The triglycerides are converted to normal paraffins by hydrotreating them in pressurized reactors to produce liquid green fuels like renewable diesel, which is chemically like petroleum-based diesel. Renewable fuels produced by hydrotreating vegetable oils are often called hydrotreated vegetable oil (HVO) fuels. Renewable diesel can be a 100% replacement for petroleum-based ultra-low-sulfur diesel. Renewable diesel produced by using renewable energy has a carbon intensity that can be 70% lower than petroleum diesel.<sup>13,14</sup>

Biodiesel is produced by reacting vegetable oils and animal fats with an alcohol like methanol or ethanol. This transesterification reaction converts the triglycerides into a mixture of alkyl (methyl, ethyl) esters of long-chain fatty acids. Biodiesel is also called fatty acid methyl ester.<sup>12</sup> It contains oxygen, has a higher cloud point and poorer cold flow properties than pe-

troleum diesel, and is limited to blending up to 20% with petroleum diesel.<sup>15</sup>

SAF made from waste cooking oil and plant oils reduces  $CO_2$  emissions by 80% vs. petroleum jet fuel. Planes can burn a mixture of 50% SAF and 50% conventional jet fuel. Testing is ongoing to increase the allowable usage up to 100% SAF.

Biomass fuels, such as ethanol, can be made from food crops like corn and sugar cane, and biodiesel can be made from soybeans. Using these feedstocks for fuel production competes with the food chain. Research to develop second-generation cellulosic fuels is continuing to use the cellulosic parts of crops (e.g., corn stover or sugar cane bagasse) to produce second-generation biofuels that will not compete with the food chain.

Microscopic algae—or microalgae growing in water—can use the sun’s energy to efficiently combine  $CO_2$  with water to create biomass through photosynthesis. The oil-rich microalgae strains can be processed into biodiesel, green diesel, gasoline and jet fuel. There is significant research exploring the usage of microal-

gae, since this route would not compete with the food chain.

Renewable natural gas (RNG)—also called biomethane—is produced from dairy farm biomass, waste food and landfills by anaerobic digestion of the organic biomass in an oxygen-free environment. The biogas produced from the anaerobic digester contains 60%  $CH_4$  and 40%  $CO_2$ . The  $CO_2$  must be removed before the RNG can be put into natural gas pipelines. Biomethane made from biomass with  $CO_2$  capture by CCS will play a role in reducing the need for natural gas. CCUS will be key in the production of biogas.

Synthetic fuels (or e-fuels) are produced by reacting green  $H_2$  made by electrolysis with captured  $CO_2$  using F-T chemistry to make hydrocarbon fuels like e-methanol, e-ethanol, e-gasoline and SAF.

**Circular economy pathway (recycled plastics, renewable feedstock and synthetic chemicals)—The petrochemical industry’s pathway to reducing Scope 3 emissions.** To reduce Scope 3 emissions, chemical producers



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must invest in the recycling of single-use plastics and must also change to renewable feedstocks to make base monomers and look at new less-carbon-intensive technologies for grassroot chemical plants.

More than 75% of plastics produced are discarded after one use and end up in landfills and oceans. In 2018, the U.S. produced 35 MMT of plastics, and it is estimated that only 9% was recycled.<sup>16</sup> The American Chemistry Council (ACC) member companies established a program called Roadmap to Reuse. The initiative's two goals were to ensure that 100% of U.S. plastics packaging will be made to be recyclable or recoverable by 2030, and to also ensure that 100% of U.S. plastic packaging will be designed to be reused, recycled or recoverable by 2040. Internationally, nearly 50 global companies have joined the Alliance to End Plastic Waste, which is an industry-supported non-governmental and non-profit organization based in Singapore. The Alliance's goal over the next 5 yr is to develop and deploy solutions to minimize and manage waste and to promote post-use solutions for plastics.

Most waste plastics end up in landfills, with only a small percentage being burned for heating value, with essentially no CO<sub>2</sub> capture. The need to stop landfilling and to begin recycling waste plastics is key to reducing Scope 3 emissions. Industry must play a key role in educating consumers and in forming partnerships with plastic recycling companies. The two primary methods for plastic recycling are mechanical recycling and chemical recycling (i.e., advanced recycling).

Mechanical recycling involves plastics collection, sorting by plastic type, cleaning, shredding, melting and re-pelletizing the plastics into new pellets. This process is very effective for single-type plastics like polyethylene (PE) and polypropylene.<sup>17</sup>

Chemical recycling is used for more complex plastics and involves breaking down the plastics to their basic components in a liquid or gaseous state for further processing. Pyrolysis and gasification are the two most common methods. Many petrochemical companies are actively working on both approaches.

Pyrolysis can convert waste plastics into plastic pyrolysis oil and plastic pyrolysis gas. After treatment and removal of oxygenates, the pyrolysis oil can be converted to diesel fuel or used as feedstock

in an ethylene cracking furnace. Companies are running tests using 5%–7% pyrolysis oil from waste PE plastic as feed to an ethylene furnace.

Gasification can convert waste plastics into syngas (CO and H<sub>2</sub>). F-T chemistry is then used to convert the syngas to methanol, ethanol and synthetic fuels, as well as into chemicals like ethylene and propylene. Gasification can occur at low pressures and high temperatures (1,000°C–1,200°C), with the syngas after cleanup containing approximately 39% H<sub>2</sub>, 43% CO, 13% CO<sub>2</sub> and 5% nitrogen.<sup>18</sup> Research at universities is ongoing to use hydrocracking to break down plastic shreds into smaller carbon molecules that can be used to produce jet fuel, diesel and lubricants. One process being developed uses supercritical water to convert waste plastics into liquids and gas that can be further refined and upgraded to produce new virgin plastics.<sup>19</sup>

In the U.S., the National Renewable Energy Laboratory (NREL) is leading efforts to study hydrogenation over catalyst to break the C-C bonds and convert the plastic polymer back into liquid alkanes like ethane that can then be used to make ethylene. The NREL is also trying to develop recyclable-by-design polymers that would have a closed-loop lifecycle. This would require designing a monomer structure that can efficiently polymerize to the desired polymer and then undergo selective depolymerization to recover the monomer.<sup>17</sup>

Industry must look at using renewable feedstocks in olefin plants to produce ethylene and propylene. Renewable naphtha and renewable diesel made from biobased sources like wood biomass or hydrotreated waste oils, fats, tall oil or tallow could be used as feed for ethylene plants. Using biofeedstocks for crackers would significantly reduce Scope 3 emissions of ethylene and its derivatives. Research is being conducted on combining pyrolysis and catalytic cracking for the direct upgrading of polyolefin pyrolysis vapors over catalysts in vapor phase to produce base chemicals (C<sub>2</sub>–C<sub>4</sub> olefins). This approach has fewer steps than the current approach of pyrolysis of plastic waste, treatment of the pyrolysis oil and then cracking it in an ethylene furnace. The process has the possibility of reducing energy requirements and CO<sub>2</sub> footprint in waste plastics recycling.<sup>20</sup>

In addition to using recycled plastics and biobased feedstocks, the chemical industry can use renewable H<sub>2</sub> and captured CO<sub>2</sub> to make synthetic chemicals (such as ethanol and methanol) and olefins (such as ethylene and propylene) by using the MTO process.

The key to success of the circular economy begins with the consumer, who must save single-use plastic bottles for recycling. The consumer is the first link in this circular economy.

**Takeaway: The seven pathways to decarbonization.** The oil and gas industry will rebrand itself as an energy provider and will transition to selling low-carbon-intensity energy like renewable wind and solar power, green and blue H<sub>2</sub>, low-carbon LNG, biofuels, renewable diesel, e-fuels, e-gasoline and SAF.

Improving energy efficiency is the cheapest way to reduce CO<sub>2</sub> emissions. For new facilities or major plant expansions, new technologies are being considered that have better energy efficiency and lower carbon intensity. For catalyst changeouts, producers should consider newer formulated catalysts for higher yields and lower energy intensity. Electrification of transportation and industry with renewable power will play key roles. CCUS will be required for processes that are hard to decarbonize.

The following is a summary of the seven pathways to decarbonization. The last three pathways support sustainability and were discussed in this article. The first four pathways supporting decarbonization will be covered in Part 2, which will be published in the June issue.

Reducing Scope 1 and Scope 2 CO<sub>2</sub> emissions includes the following:

- 1. Energy efficiency:** Improving energy efficiency of facilities, building new more efficient facilities, and maintaining energy recovery equipment. Producers should stop routine flaring and should minimize flaring at startup and shutdown. Companies should also use drones to detect and track methane leaks.
- 2. Technology:** Using new processes and catalysts to improve yields and reduce energy intensity.
- 3. Electrification:** Electrifying process equipment by using renewable electric power (e.g.,

wind, solar, hydro and nuclear). This includes investing in, utilizing and selling renewable power, as well as investing in battery storage.

4. **CCUS:** Utilizing cost-effective CCUS of captured CO<sub>2</sub>. Producers should join regional CCUS networks for economy of scale and use captured CO<sub>2</sub> in their production of e-fuels.
5. **Green and blue H<sub>2</sub>:** Producing, using and selling low-carbon H<sub>2</sub>, and utilizing H<sub>2</sub> as an energy carrier.
6. **Low-carbon fuels:** The oil and gas industry's pathway to reduce Scope 3 emissions is producing and selling energy products with low carbon intensity, such as:
  - Biofuels and renewable fuels (e.g., renewable diesel and SAF)
  - Synthetic fuels (P2X), such as e-fuels and e-gasoline made from green H<sub>2</sub> and captured CO<sub>2</sub>
  - Low-carbon LNG through CCS on natural gas feed and the electrification of LNG plant compressors
  - Renewable electricity like wind (onshore/offshore) and solar PV electricity
  - Green and blue H<sub>2</sub>.
7. **Circular pathway:** The pathway to reduce Scope 3 emissions for the petrochemical industry includes the following:
  - **Recycle waste plastics:** Minimizing the circular carbon cycle by either mechanical reprocessing or chemical recycling (pyrolysis, gasification) waste plastics
  - **Use renewable feedstocks:** Using bio-naphtha, hydrogenated vegetable gasoil (diesel) and plastic pyrolysis oil to produce the base chemicals ethylene and propylene
  - **Make synthetic chemicals:** Producing ethanol and methanol using renewable H<sub>2</sub> and captured CO<sub>2</sub>.

The good news is that the oil and gas and petrochemical industries have the technology and assets needed for offshore wind, blue/green H<sub>2</sub> production, and CO<sub>2</sub> capture and storage, and have refinery units and technology available to produce renewable fuels. Industry is pre-

pared to begin the energy transition journey to a lower-carbon world.

**Part 2.** In the June issue, Part 2 of this article will cover the first four pathways to decarbonization: energy efficiency, new technology, electrification and CCUS (including uses of CO<sub>2</sub>) **HP**.

#### NOTE

<sup>a</sup> Calculated using the LHV of methane of 21,500 Btu/lb; 1 mol CH<sub>4</sub> burns to 1 mol CO<sub>2</sub>

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## Biofuels, Alternative Fuels and Green Petrochemicals

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# MVR compressor key to steam energy upgrade at Terneuzen polyolefin plant

Reducing energy costs and creating more sustainable local energy sources are common challenges across many industry sectors. Dow Chemical's process plant in the Dutch municipality of Terneuzen requires a considerable amount of energy, often in the form of steam. Tasked with the challenge of finding a solution that would reduce its energy use, engineers focused on the untapped potential of low-pressure steam.

In an ongoing pilot project, the plant uses mechanical vapor recompression (MVR) to upgrade low-pressure steam and reuse it to supply energy. Central to the plant's MVR solution at Terneuzen is a two-stage centrifugal compressor, which compresses superheated steam from 3 barg to 12.5 barg in two steps. The result has been a reduction in natural gas usage of around 10 million normal cubic meters (MMNm<sup>3</sup>) in the last 12 mos and a net reduction in carbon dioxide (CO<sub>2</sub>) emissions of 17.8 kilotons (kt).

**Power to products: Electrification and flexibility.** In 2014, the Dutch government initiated the "Power to Products" project. Various companies from the process industry, energy suppliers, network operators and technology partners came together to work on the initiative. The project needed to address three interrelated central points: how (technically, operationally and organizationally), at what cost and under what conditions could the process industry make its electricity demand more flexible. The aim was to allow the process industry to use cheap renewable electricity (wind and

solar) and, simultaneously, contribute to grid stability. How this would be carried out and under what conditions were the underlying themes of the project.

The concept is straightforward. With the introduction of more renewable energy sources, the supply of sustainable electricity would increase on windy and/or sunny days. However, if the electricity demand was low at such times, the price would likely also be low, sometimes lower than the gas price, and on occasion nearly zero. The process industry could then take advantage of this low power price. With little wind or solar energy, the power price would increase; during these times, the industry could reduce its electricity demand and contribute to the balance of supply and demand.

How can the process industry achieve this? The answer is twofold and revolves around providing increased electrification and greater flexibility. The first is electrification, meaning the industry will use electricity instead of fossil fuels, such as natural gas. The second is flexibility, which means that the process industry can offer control of power requirements.

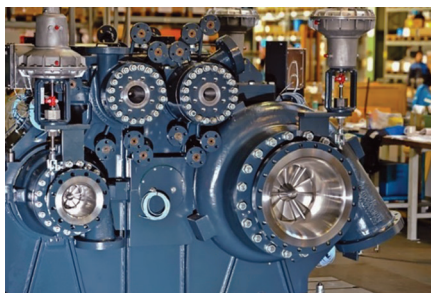


FIG. 1. Integrally geared compressor.

The process industry can do this in two possible ways. One is by storing energy during cheaper periods in the production of chemical products and intermediates such as hydrogen, pressure, heat or cold thermal storage via charging and discharging. They would then use the stored products during more expensive periods. The second method is to temporarily reduce production and power demand at expensive times and catch up later when the price has decreased. In this method,

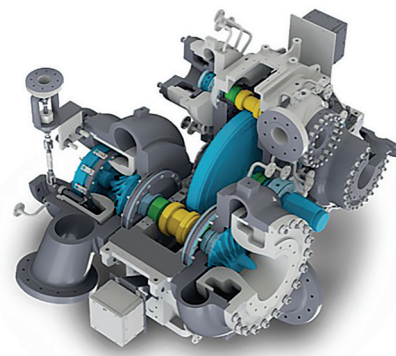


FIG. 2. Cross-section of an integrally geared compressor core.

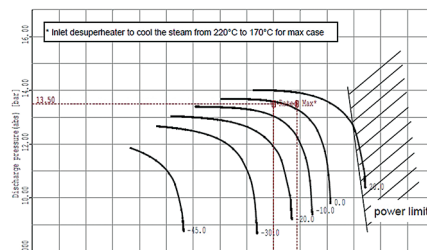


FIG. 3. Performance map for turbocompressor using inlet guide vanes.

the industry can reduce the demand for fossil fuels and reduce CO<sub>2</sub> emissions, making the overall energy supply more sustainable and cost-efficient.

#### Mechanical vapor recompression.

Dow Chemical participated in the “Power to Products” project and chose to focus on MVR. MVR, or in this case steam recompression, is a good example of the electrification of industrial energy demand. It is also highly energy-efficient because the residual heat is upgraded to high-quality heat.

Dow Chemical was drawn to MVR technology because of the availability of low-pressure steam at its Terneuzen polyethylene processing plant, even though the supply is not constant—especially during winter, when it is needed to heat buildings and for steam tracing. In contrast, there is excess when the plant is running steam turbines or when buildings are not heated during the summer. Typically, Dow Chemical condenses excess low-pressure steam, and the water is sent to the boiler to create high-pressure steam.

In 2015, Dow Chemical collaborated on a feasibility study, executed by a con-

sulting company<sup>b</sup> to use MVR to convert heat from condensation to efficient energy. Research revealed that there were companies that already used MVR but at a low-pressure level (1 bar–2 bar), such as in the food or paper industries for heat recovery. In most cases, the companies used blowers. However, the Terneuzen plant required higher pressures than these blowers could achieve.

Dow Chemical contacted several compressor manufacturers to explore the potential of supplying the requisite equipment for MVR. The equipment partners suggested were between bearing centrifugal compressors, reciprocating compressors and integrally geared centrifugal compressors (IGC). As a result of these preliminary investigations, various alternative feasibility studies were conducted to analyze technical and economic potential (FIG. 1).

The polyethylene (PE) plant at Terneuzen uses water for reactor cooling. At the end of the process, the cooling water becomes low-pressure steam. Especially during the summer, the demand for heating is lower, which in some periods means that part of the low-pressure steam from

the PE plant cannot be used and must be sent to the atmosphere or condensed. During the initial research phase, it became clear that MVR could be a good solution to avoid this waste of energy by uprating the steam to 12.5 barg or 35 barg.

Considering the low energy prices at that time, the result of the 2015–2016 feasibility study showed that the MVR project was less economically feasible for the smaller flowrates, such as with Case 1 at 10 tons per hour (tph) (TABLE 1). From an economic viewpoint, the most viable case studies were those with 50 tph, with Case 3 typically representing the most feasible. However, Dow Chemical wanted to test the MVR technology on a small scale, with the prospect of possibly including the technology in future PE expansion projects.

Therefore, the key to deciding which of the many case studies to use for the MVR pilot project was to base the selection on the preferred steam pressure level rather than a more attractive flowrate. In this case, it meant using the low-pressure steam from the reactor cooling water that supplies the 3.5 barg grid. This is used primarily for process heating purposes and upgrading it to the lowest pressure level, which would result in less firing of the auxiliary boilers and reduce fossil-fuel usage. For this reason, even though 3.5 barg (10 tph) was economically less attractive, the lower pressure provided the best conditions for the pilot’s primary aim. The MVR pilot project got underway in 2018.

**Selecting integrally geared compression for MVR.** MVR is an open-heat pump system, and it requires a relatively small amount of energy to increase compression pressure and temperature. Several compressor manufacturers mentioned in the feasibility study could produce a suitable compressor, but after a detailed evaluation, the co-authors’ company<sup>a</sup> was awarded the order. The company<sup>a</sup> has more than 30 yr of experience in the steam compressor field and can design each compressor to meet specific process and control requirements.

The company<sup>a</sup> was chosen primarily for its proposed solution for an integrally geared centrifugal compressor, with its key characteristic of an overhung arrangement of the impellers on the pinion shaft ends. One pinion shaft is designed for one or two opposing compressor stages. In this ar-

**TABLE. 1.** Five potential cases for a future pilot from the 2015–2016 feasibility study

Parameter	Units	Case 1	Case 2	Case 3	Case 4	Case 5
Capacity	tph	10	50	50	50	10
P1	bara	4.2	4.2	13	4.2	4.2
T1	°C	150	150	195	150	150
P2	bara	13.3	13.3	36	36	36
T2	°C	240	240	340	340	340



**FIG. 4.** The compressor installation inside the Terneuzen plant.



rangement, separate compressor bearings are not necessary. The bearings of the pinion shafts are identical to those of the compressor rotor. The rotor shafts are made from a single heat-treated forged low-alloy steel. Shaft seals can be labyrinths, dry gas seals or floating carbon rings.

The high-speed rotors use tilting pad bearings and sleeve bearings for the slow-speed shaft, while multiple disk couplings connect the driver and the compressor gearbox. Operational control is via a fixed-speed e-motor drive with inlet guide vanes installed upstream of the first stage impeller (part of the compressor casing).

The integrally geared compressor features optimized aerodynamic speed capability, increasing rotor speeds along the compression process. Furthermore, its integral setup makes it possible to have an intercooling or steam application for a desuperheater after each compression stage, which results in increased efficiency (FIG. 2).

This IGC provides reliability, an essential element in polyethylene plants. The broadening use of this compression technology in hydrocarbon processing environments has been supported by several factors, including advances in shaft seal technology, modern aerodynamics, increased rotor dynamic and thermodynamic knowledge. With these advances, its simplicity, reliability, and lightweight and compact design, IGCs have become more widely accepted in the hydrocarbon world.

**Design details.** For the Terneuzen PE plant, a two-stage compressor was designed (FIG. 4), which means one pinion with two impellers on each end. The number of stages is defined by the pressure ratio limit for each stage; if required, it would have been possible to design a three-stage compressor for this purpose. The advantage would have been a lower power consumption of the e-motor (though not to a significant degree).

The MVR is a two-stage IGC that compresses superheated steam from 3 barg to 12.5 barg. The nominal mass flow of the installation is 12 tph. The steam is cooled by water injection with a desuperheater at the inlet and between the stages. The larger droplets are caught downstream by a knockout drum. The steam enters the compressor on the suction side at 3 barg and a temperature of 150°C–220°C. The steam is sent through the desuperheater

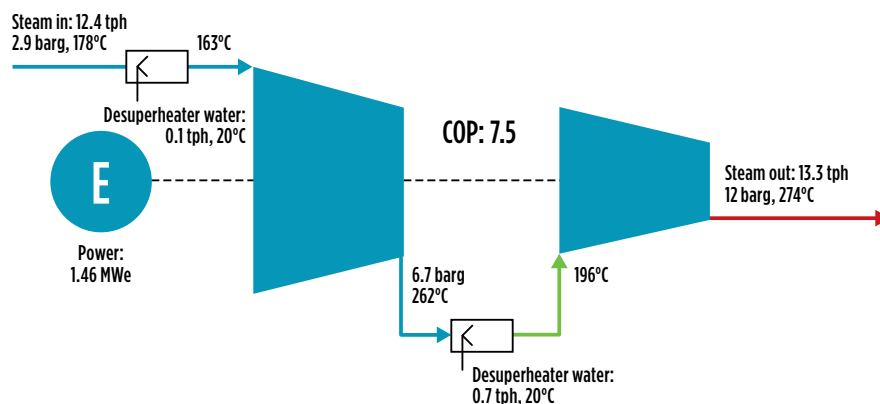


FIG. 5. Average unit values between November 17, 2020 and November 17, 2021.

and the knockout drum in case temperatures reach higher than 170°C so that it can avoid higher temperatures in the compressor discharge stage (FIG. 3).

### High coefficient of performance.

The co-author of this article<sup>b</sup> carried out research on the compressor's coefficient of performance (COP) that was performed once the compressor was up and running. The research determined a result of 7.5, which represents a high performance—partly attributable to the inherent advantage of an open-heat pump compared to a standard compression heat pump (FIG. 5). More recently, between November 17, 2020, and November 17, 2021, the measurements resulted in an overall COP of 7.5. A COP of 7.5 means that for 1 MW of electricity, 7.5 MW of thermal energy was produced.

The COP value indicates the energy efficiency of a range of machines, such as chillers, heat pumps and MVRs. In simple terms, COP shows the ratio between the recovered thermal power and the supplied electrical compressor power. Depending on the application, a COP value of at least 2 can be attractive from an energy and economic perspective. After reaching a COP high of 7.5, the expectations on the potential of steam compression are certainly high. In addition to good COP achievement, steam recompression underpins natural gas savings and CO<sub>2</sub> emissions reductions.

Using the untapped potential of low-pressure steam via MVR, the Terneuzen plant operators successfully found a more energy-efficient and sustainable energy supply. The project highlighted that MVR can be used anywhere where there is low-pressure steam.

The compressor now operates without significant problems, and it has only been briefly out of service for steam network maintenance. In the last 12 mos, approximately 10 MMNm<sup>3</sup> of natural gas was saved, and a CO<sub>2</sub> reduction of 17.8 kilotons was achieved. **HP**

### NOTES

<sup>a</sup> Atlas Copco Gas and Process

<sup>b</sup> Blue Terra



**ULRICH SCHMITZ** has more than 25 yr of experience in sales, marketing and project handling of tailor-made turbomachinery for markets such as industrial gases, power generation, chemical/petrochemical, and oil and gas.

As Vice President Marketing for Atlas Copco Gas and Process, he is based at the production company Atlas Copco Energas in Cologne, Germany. Mr. Schmitz drives product management and state-of-the-art products while also identifying new markets and products needed in the near- and long-term future. He holds a diploma in mechanical engineering from the University of Applied Sciences in Cologne (FH Köln), Germany.



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**RENÉ WAGGEVELD** has 18 yr of industry experience and has spent 13 yr with BlueTerra. His expertise is in process modeling, capacity expansion studies, and energy optimization projects in various fields, ranging from petrochemical companies to paper and energy production. Dr. Waggeveld earned an MS degree in chemical engineering from the University of Twente, the Netherlands, and a PDEng in process design from the same university.

# Quickly screen catalysts for hydrotreating of vegetable oil using high-throughput micro-pilot plants

Accurate catalyst evaluation is an important step in optimizing catalytic processes with respect to product yield, energy efficiency and overall product quality. High-throughput catalyst testing and small-scale reactors offer several advantages when compared to larger reactor systems.

Using reactors of smaller scale to evaluate catalysts with renewable feedstocks presents a clear advantage: smaller volumes reduce the amount of feed required, avoiding the typical issues associated with obtaining large quantities like handling, shipping and storage (also for longer-term availability of reference feed material). Overall, small-scale parallel reactor systems like the unit described here are more cost effective than large-scale reactors.

The author's company continuously evaluates the feasibility of processing new feedstocks in its proprietary systems<sup>a</sup>. In this article, the results of processing blends of soybean oil and straight-run gasoil (SRGO) and 100% vegetable oil (VO) for renewable diesel production are presented.

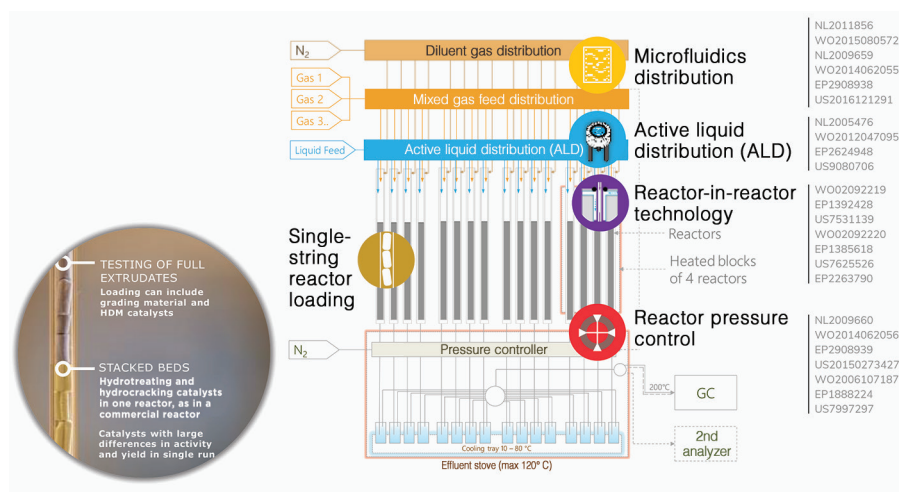
In this testing program, a commercial ultra-low sulfur diesel (ULSD) NiMo catalyst was used to hydrotreat the VO.

## METHODOLOGY

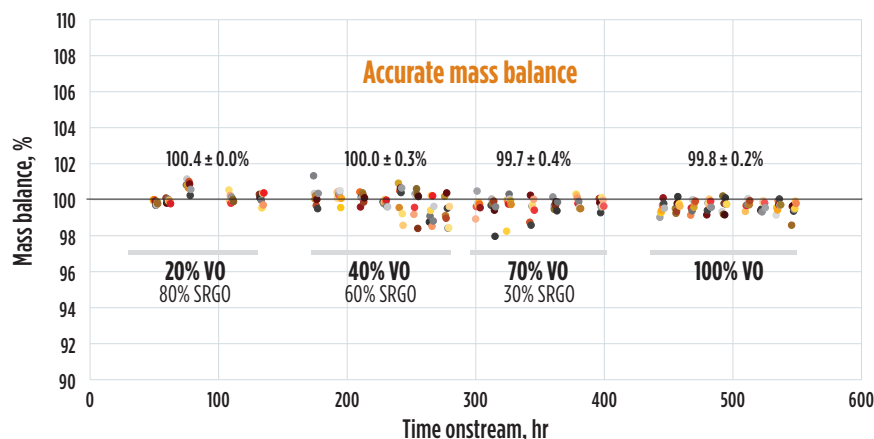
**The micro-pilot plant.** This testing program was conducted in a 16-parallel fixed bed reactors system with a diameter of 2 mm–2.6 mm. **FIG. 1** shows a schematic overview of the 16-parallel reactors micro-pilot plant. This unit employs a proprietary high-throughput catalyst testing system<sup>a</sup> that enables the tight control of process conditions: temperature, flow-rates and pressure.

The testing program was performed in collaboration with a global market-leading catalyst supplier. For this program, only eight reactors were used—the high-throughput 16-reactors system allows for the selective isolation of unused reactors.

**Reactor loading.** The catalyst packing in the single-pellet-string reactors (SPSR) is straightforward and does not require special procedures. A single string of catalyst particles is loaded in the reactors with an internal diameter (ID) that closely



**FIG. 1.** Schematic of proprietary 16-parallel reactors for configured hydoprocessing applications. More information can be found in the several patents.



**FIG. 2.** Mass balance for all feedstocks tested (colors varied by reactor).

matches the particle average diameter. To enhance hydrodynamics, an inert nonpo-

with two different bed lengths to test two different liquid hourly space velocities

No plugging was observed in any of the small-scale reactors during the 23-d test. The high-throughput 16-parallel reactors system offers a reliable testing platform to quickly screen new catalysts for the production of renewable fuels.

rous diluent material (with a defined average particle size distribution) is used as a filler. Before conducting the final loading in a steel reactor tube, a trial loading is often performed in quartz reactors to confirm the packing (FIG. 1). The extrudates are not sorted for length or otherwise.

**Operating conditions.** A commercial ULSD NiMo catalyst was loaded in eight reactors (561-mm length and 2-mm ID)

(LHSVs) simultaneously. All reactors were tested at 70 barg pressure.

**Feedstock.** Pressure drop is one of the main challenges when processing vegetable oils in hydroprocessing units. This is even more evident when using pilot plants with small-diameter reactors, as catalyst fouling can quickly lead to plugging. For this reason, the approach of this test was the co-feeding of the vegetable

oil (soybean oil, see properties in TABLE 1) blended with an SRGO at different ratios, as shown in TABLE 2.

TABLE 2 lists the different feed blends tested over a period of 400 hr onstream (HOS) and 100% VO over 150 hr (6 d). The feed blends with 70% VO and 100% VO were spiked with dimethyl disulfide (DMDS) up to 2 wt% sulfur.

## RESULTS

**Mass balance.** Mass balance calculations ensure that the metered flows used in the calculations are accurate. An accurate mass balance is an internal control of the data quality obtained.

When calculating mass balance, various accurate measurements from both online and offline analytical equipment are composed together to accurately measure mass balance. Inherently, system errors from feed distribution to analytics require some consideration in interpreting the reported data. The main difference is that, compared to a single reactor, the distribution of liquid (i.e., the LHSV) across all the reactors has a relatively large impact on the recorded mass balance. FIG. 2 shows the overall mass balance for all reactors and the different feed blends.

The mass balance calculation includes the water in the gas stream measured with the online gas chromatograph (GC). Using the GC to measure the water content in the effluent gas is a reliable method for closing the mass balance. The gas-liquid separator was operated at optimized con-

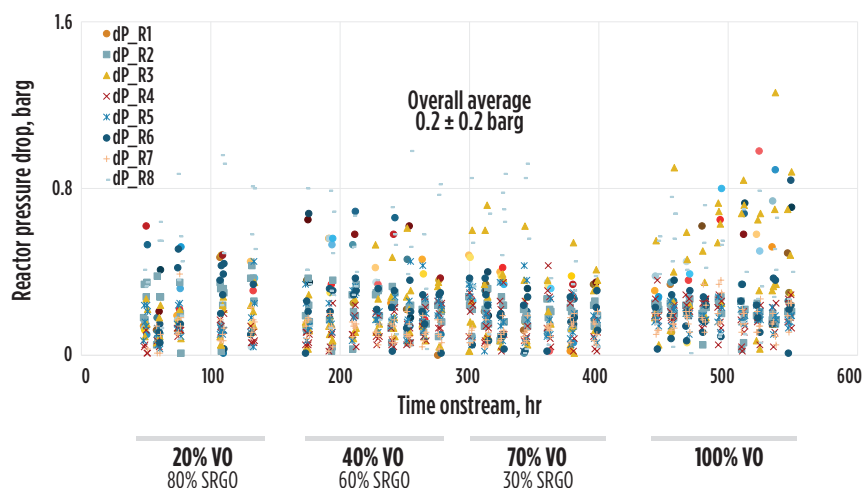


FIG. 3. Pressure drop for all eight reactors for all feedstocks tested (colors varied by reactor).

TABLE 1. Product sulfur at ULSD conditions for two VO blends

Condition	LHSV = 1 l/l/hr	LHSV = 1.5 l/l/hr
40% VO	3.3 ± 0.7 ppmw S	35.2 ± 3.0 ppmw S
70% VO	4.6 ± 0.7 ppmw S	86.4 ± 2.8 ppmw S
100% VO	1.5 ± 0.2 ppmw S	2.6 ± 0.5 ppmw S

TABLE 2. Feedstocks tested

HOS	Feed	Description
0–60	SRGO	Line out
61–110	20% VO + SRGO	20% VO testing
111–278	40% VO + SRGO	40% VO testing
279–400	70% VO + SRGO	70% VO testing
400–550	100% VO	100% VO testing

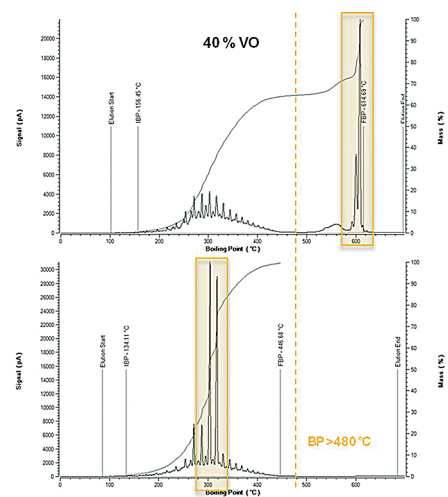


FIG. 4. Example SimDis for 40% VO feedstock (above) and the liquid product (below).



ditions during the test to evaluate the effect in the overall mass balance.

### Reactor pressure regulation and pressure drop over the reactors.

Reactor pressure regulation is not only important to ensure accurate pressure control at operating pressures, but also to help maintain equal distribution of the inlet flow over all reactors.

The catalyst testing system<sup>a</sup> includes a microfluidic-based reactor pressure controller (RPC). This patented pressure-regulation technology enables the individual regulation of the backpressure of each separate reactor at the targeted setpoint, allowing the most accurate and stable pressure control in a multi-parallel reactors system, with an average reactor-to-reactor pressure deviation of < 0.1 barg.

Since the RPC measures the inlet pressure of each reactor, it can maintain a constant inlet pressure by regulating the backpressure. As a result, the distribution of the inlet flows over the reactors is unaffected and a low reactor-to-reactor flow variability is achieved. This also allows the measurement of pressure drop over the reactors. FIG. 3 shows the pressure drop obtained for all reactors during the test; it can be seen that the pressure drop for all reactors is very small with an overall average of 0.2 barg.

**VO conversion.** At the predefined testing conditions, a total conversion of the VO was obtained without obvious effect on the LHSV. No deactivation of the catalyst was apparent with the complete test duration. FIG. 4 shows an example simulated distillation (SimDis) for the 40% VO feedstock where the conversion of triglycerides (BP > 480°C) into paraffins (apparently mostly C<sub>16</sub> to C<sub>18</sub>) can be seen.

**Liquid product yields.** FIG. 5 presents the diesel, kerosene and naphtha yields for 40% VO, 70% VO and 100% VO feedstocks. Key findings include:

- The yield to diesel is ~80% for the 100% VO feedstock
- Liquid product analysis (ASTM D5291) confirmed that there was no oxygen left
- As expected, no naphtha or kerosene was produced from the conversion of the VO; there is a direct conversion of

- triglycerides to C<sub>12</sub>+ paraffins
- Small effect of the higher LHSV (1.5 l/hr) on the VO products yield
- Overall a good reactor-to-reactor repeatability for the product yields.

**Gas product yield.** FIG. 6 shows the gas make yield (C<sub>1</sub>, C<sub>3</sub> and C<sub>4</sub>) for all feed-

stocks tested [only traces of C<sub>2</sub> were observed (not presented in the graph)]:

- As expected, methane (CH<sub>4</sub>) and propane (C<sub>3</sub>H<sub>8</sub>) are the main gas hydrocarbons products
- Increasing gas product yields as the amount of VO is increased on the feed
- Up to 5 wt% C<sub>3</sub>H<sub>8</sub> produced

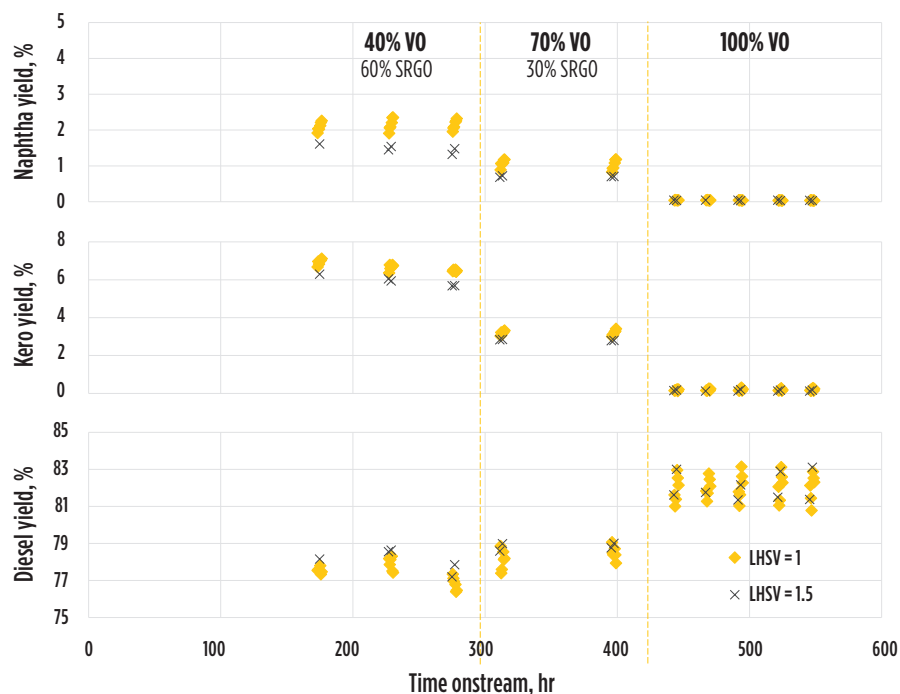


FIG. 5. Liquid product yields.

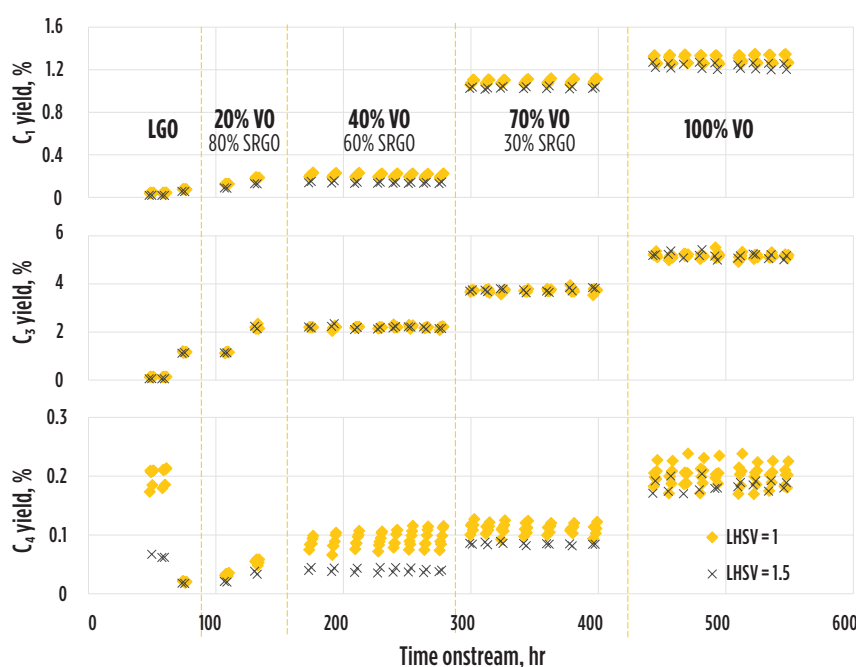


FIG. 6. C<sub>1</sub>, C<sub>3</sub> and C<sub>4</sub> gas product yields.

- when processing 100% VO
- Good reactor-to-reactor repeatability for the gas product yields
- Small but consistent effect of LHSV on the gas yields.

**FIG. 7** shows the carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) yields:

- Increasing gas product yields as the amount of VO increases
- Up to 3 wt% CO and 5 wt% CO<sub>2</sub> produced when processing 100% VO
- The yield to water presented does not include the small amount of water remaining in the liquid product

- Good reactor-to-reactor repeatability for the gas product yields
- Clear differences in CO and CO<sub>2</sub> yield when using a higher LHSV.

**Hydrogen (H<sub>2</sub>) consumption.** H<sub>2</sub> consumption was measured using the on-line GC by comparing the outlet flow of H<sub>2</sub> with the inlet flow. **FIG. 8** shows that a step increase in the H<sub>2</sub> consumption can be expected with an increasing amount of VO in the feedstock:

- Approximately 20% of the H<sub>2</sub> fed into the system is consumed when processing the 100% VO feed
- Good reproducibility for H<sub>2</sub> consumption among

duplicate reactors

- Clear effect of LHSV on the light gasoil (LGO) and LGO blends hydrotreating.

**Product sulfur.** The product sulfur was measured for the 40%, 70% and 70% VO blends at ULSD conditions. Note the very good repeatability of the sulfur results for the duplicate reactors at such high conversion:

- The reactors' temperature was adjusted to produce < 5 ppmw sulfur for the LHSV = 1 l/l/hr
- Very good reproducibility for product sulfur among duplicated reactors.

**Takeaways.** No plugging was observed in any of small-scale reactors during the 23-d test with various VO blends and 6 d of running 100% VO. Quantifying the amount of water in the gas effluent using an online GC is a feasible method for closing the mass balance. The accuracy of the mass balance and yields obtained during the test are similar to conventional hydroprocessing catalyst testing. High-temperature SimDis is a feasible method for evaluating the conversion of triglycerides during VO hydrogenation tests. The test allowed accurate measurement of the hydrodesulfurization (HDS) capacity of the catalyst at start-of-run (SOR) conditions when processing LGO / VO blends.

The proprietary high-throughput 16-parallel reactors system<sup>a</sup> produces consistent and reliable high data quality with excellent reactor-to-reactor repeatability for the hydrotreating of VO, and offers a reliable testing platform to quickly screen new catalysts for the production of renewable fuels. **HP**

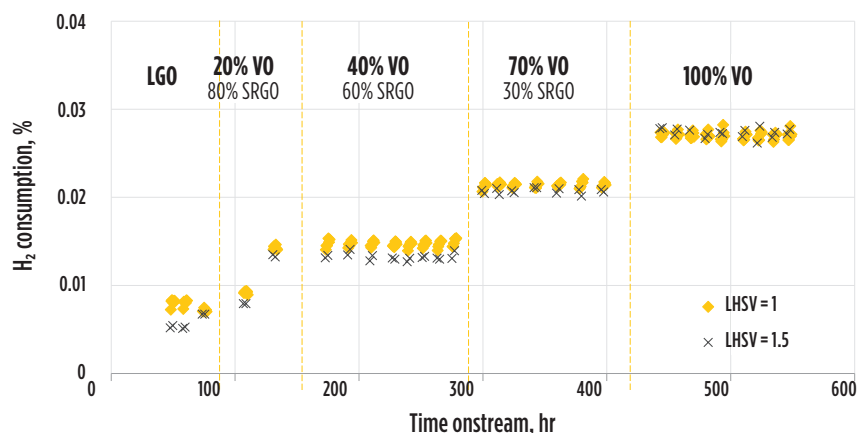
#### NOTES

<sup>a</sup> Avantium Catalysis' Flowrence® systems.

**TIAGO VILELA** leads the Refinery Catalyst Testing (RCT) global services for Avantium Catalysis and is accountable for the overall performance of the business line. Dr. Vilela has more than 19 yr of experience in engineering, project management, management consultancy and business development. Before joining Avantium, he worked as a Senior Asset Management Consultant for Jacobs and as a Management Consultant for AP-Networks. He has advised on numerous projects and maintenance turnarounds around the globe, helping clients to improve their project, turnaround and operational readiness performance. Dr. Tiago holds an MS degree in chemical engineering from the University of Aveiro, Portugal, and a Professional Doctorate in Engineering degree from Delft University of Technology.



**FIG. 7.** H<sub>2</sub>O, CO<sub>2</sub> and CO gas product yields.



**FIG. 8.** Online H<sub>2</sub> consumption.

## CO<sub>2</sub> energy recycling approach in the petrochemical industries

Many industrial processes can generate carbon dioxide (CO<sub>2</sub>) from fossil fuels. Recently, these processes have contributed to an average annual release of more than 30 Btpy of CO<sub>2</sub> into the environment. From a pre-industrial level of ~270 ppm, the concentration of CO<sub>2</sub> in the atmosphere has now surpassed the 400 ppm mark, resulting in today's observed climate change phenomena and the necessity to recover CO<sub>2</sub> from the environment. **FIG. 1** depicts the average CO<sub>2</sub> emissions to the atmosphere in the last 5 yr. The contribution of the major fuels to these emissions are:

- Natural gas: 23%
- Petroleum: 42%
- Coal: 35%.

To mitigate the CO<sub>2</sub> impact of fossil oil combustion, carbon capture and sequestration (CCS) techniques from industrial plants are being considered and implemented.

The primary processes involve partial CO<sub>2</sub> capture, compressing it for transportation via pipelines, ships, etc., and pumping it for oil recovery or other limited applications. This requires increased construction costs, fuel use and utility consumption, which inevitably produce more pollutants.

Serious concerns have been associated with these uneconomical processes, which have not solved the environmental problems posed by CO<sub>2</sub> emissions. Therefore, capturing CO<sub>2</sub> from process plants and power generation systems has been recognized as one of the most promising strategies for reducing CO<sub>2</sub> emissions and utilizing CO<sub>2</sub> as an alternate carbon source for the chemical supply chain.

Conversely, growing fuel consumption in developing countries is continuously increasing CO<sub>2</sub> concentrations around the globe. This means that the traditional reduction routes are insufficient to mitigate CO<sub>2</sub> concentrations to a permissible level. **TABLE 1** shows the main uses of CO<sub>2</sub> in the chemical industries (in 2019).

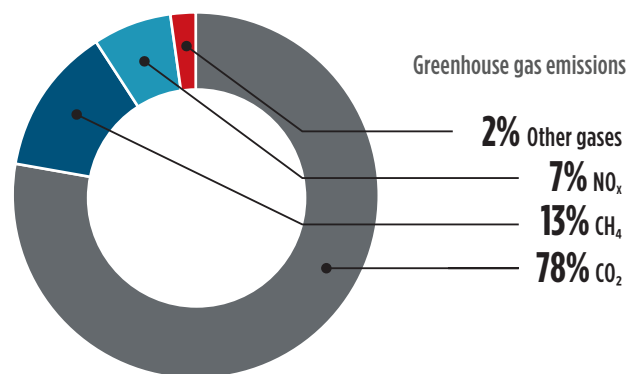
Three stages of CO<sub>2</sub> utilization developments are considered: existing mature technologies, such as urea production; emerging technologies, such as formic acid or other single carbon (C<sub>1</sub>) chemicals manufacture; and innovative explorations, such as electrocatalytic ethylene production.<sup>1,2,3,4</sup> Basically, CO<sub>2</sub> conversion reactions can be summarized as:

- CO<sub>2</sub> reduction
- CO<sub>2</sub> insertion
- CO<sub>2</sub> condensation
- CO<sub>2</sub> addition.

However, on an energy level basis, such reactions can be classified as:

- Reactions that do not require a substantial amount of external energy. Here, the reaction takes place by attaching the whole CO<sub>2</sub> moiety to the other reactant. Such reactions are often named as carboxylation reactions [e.g., the production of carbamates (R<sub>1</sub>R<sub>2</sub>NCOOR<sub>3</sub>), ureas (RRNCONRR), isocyanates (RNCO) and carbonates (ROC(O)OR)].
- Reactions that produce reduced forms of CO<sub>2</sub>. These reduction reactions naturally require a considerable amount of external energy. They include products such as: HCOO (formates), [C(O)O]2 2e (oxalates), H<sub>2</sub>CO (formaldehyde), etc.

The application of a CO<sub>2</sub> recycling approach in modern petrochemical complexes has shown great potential in the exploitation of CO<sub>2</sub> recycling reactions from process plants (e.g., methanol, ethylene and ethylene oxide) to obtain value-added products while also contributing to CO<sub>2</sub> fixation.



**FIG. 1.** The average CO<sub>2</sub> emissions in the last 5 yr.

**TABLE 1.** Main uses of CO<sub>2</sub> in the chemical industries, 2019

Process	Production, tpy
Urea	140
Inorganic carbonate	75
Methanol	18

**CO<sub>2</sub> as a chemicals building block.** In principle, the utilization of CO<sub>2</sub> as a chemicals building block applies CO<sub>2</sub> catalytic hydrogenation. The simplest C<sub>1</sub> liquid product is methanol (CH<sub>3</sub>OH), which can be easily obtained from recycled CO<sub>2</sub>. When capitalizing on CO<sub>2</sub> as a C<sub>1</sub>-building block in industry, its low energy level is certainly a major barrier. However, high-energy co-reactants [e.g., hydrogen (H<sub>2</sub>), unsaturated compounds or strained cyclic molecules] must be used.<sup>5</sup>

Consequently, the overall energy balance and the primary source of energy employed to generate the starting materials are carefully evaluated to assess the net effect of envisaged CO<sub>2</sub> utilization.

Three main routes are the basis of recycled CO<sub>2</sub> synthesis:

- Heterogeneous catalysts, based on the metal complexes of CO<sub>2</sub>, are commonly applied in CO<sub>2</sub> conversion processes in petrochemical industries [e.g., the production of dimethyl carbonate, synthesis gas (CO, H<sub>2</sub>) and methanol synthesis].<sup>6,7</sup>
- Electrochemical activation of CO<sub>2</sub> can result in the production of a number of valuable petrochemical products, such as methanol, ethylene (C<sub>2</sub>H<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), and other hydrocarbons and oxygenates.

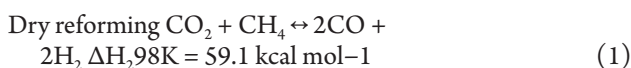
Photocatalysts application is also used to enhance a chemical reaction, producing valuable products, such as carbon monoxide (CO), methanol, C<sub>2</sub>H<sub>5</sub>OH, methane (CH<sub>4</sub>), and higher hydrocarbons.<sup>8</sup>

The application of nanocarbons (carbon nanotube, graphene oxide, etc.) possessing high thermal conductivity, high theoretical specific surface area, unique carrier mobility and an sp<sup>2</sup>-hybridized carbon configuration, have shown promotion to CO<sub>2</sub> photocatalysis applications. Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is applied successfully for improved photocatalytic activity.

## MAIN APPLICATIONS OF RECYCLED CO<sub>2</sub> IN PETROCHEMICAL PLANTS

As has been discussed previously, CO<sub>2</sub> recycling is under increasing scrutiny as one of the most important approaches to mitigate CO<sub>2</sub> emissions to the environment, as well as to find a low-cost carbon source. The main applications of recycled CO<sub>2</sub> in the petrochemical industries are discussed here.

**CO<sub>2</sub> reforming of methane.** The production of value-added chemicals by combining CH<sub>4</sub> and CO<sub>2</sub> molecules has always been attractive. The process is called “dry” reforming, indicating the reaction between an equimolar amount of CO<sub>2</sub> and CH<sub>4</sub> giving a 1:1 ratio of CO and H<sub>2</sub> (S = 1). In this endothermic reaction, CH<sub>4</sub> adsorbs on a noble metal [such as platinum (Pt)], whereas CO<sub>2</sub> adsorbs on a support. The reaction is conducted on Ni/MgO or Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst at temperatures from 800°C–1,000°C (1,472°F–1,832°F), calculated in Eq. 1:



The advantages of dry reforming are that it utilizes very cost-effective raw materials, and that one molecule of CO<sub>2</sub> is used for each CH<sub>4</sub> molecule, making the process even more attractive. However, the process suffers from coking, and the context

of methanol production is the low H<sub>2</sub>/CO (S = 1) ratio in the product gas, which is not suitable for methanol synthesis.<sup>1,2,4</sup>

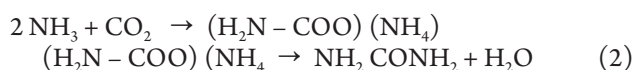
**Hydrogenation of CO<sub>2</sub> to methanol.** A potential use of CO<sub>2</sub> exists as an alternative feed in place of CO methanol production. CO<sub>2</sub> hydrogenation to produce methanol is accompanied by a simultaneous reverse water-gas-shift reaction. In this process, the methanol formation is an exothermic reaction and the molecular weight of the carbon-containing molecule decreases. Hence, the thermodynamics foresee a decreased temperature and an increased pressure for selectivity.

The accompanying reverse water-gas shift reaction is undesirable as it consumes H<sub>2</sub>, resulting in a decreased yield of methanol. In the meantime, the large amount of water produced by both reactions has a certain inhibitory effect on the catalyst, leading to its eventual deactivation—therefore, catalyst selectivity has critical importance. Recent processes for CO<sub>2</sub> hydrogenation reaction apply ternary CuZnAl oxide catalyst with additional modifiers and carbides.

**Bi-reforming of methane for methanol production.** This process is utilized for methanol synthesis through syngas production—H<sub>2</sub>:CO (S ≈ 2) can be achieved by a selective process, termed “bi-reforming,” a combined steam reforming and dry reforming process of methane giving exclusively syngas, the needed feed for subsequent methanol synthesis. The bi-reforming of methane is also a practical procedure for natural gas that contains CO<sub>2</sub>.

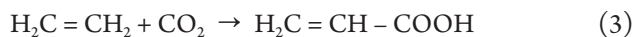
Bi-reforming compared to methane dry reforming (MDR) exclusively provides the 2H<sub>2</sub>/CO ratio; the fact that similar catalysts active for steam reforming or dry reforming (Ni/MgO at 800°C–1,000°C) can be used is also an advantage.

**Urea, formaldehyde and melamine.** Urea synthesis is a major process utilizing CO<sub>2</sub> (Eq. 2):



The CO<sub>2</sub> conversion/fixation potential is the incorporation of CO<sub>2</sub> as a C<sub>1</sub> source, such as UF-resins and MF-resins, which are used in many applications (wood additives, electrical insulators, etc.).

**Acrylates synthesis.** Sodium acrylate is a basic intermediate for polyacrylate production (Eq. 3):



For acrylate synthesis, the catalytic pathway includes nickel lactones.

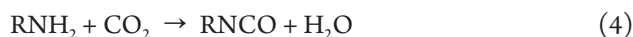
**Carbonate syntheses.**

- Monomeric carbonates: Carbonates are becoming an industrial viable alternative to toxic phosgene (COCl<sub>2</sub>). An example is the carbonation of ethylene oxide, as opposed to phosgenation of ethylene glycol for ethylene carbonate synthesis. These carbonates are used in producing polycarbonates.
- Dimethyl carbonate: Dimethyl carbonate (DMC) is a linear carbonate and is produced by the



cycloaddition of CO<sub>2</sub> to an epoxide. Its industrial uses include solvents and transportation of fuel oxygenates.

**Polyurethanes synthesis.** Polyurethanes are normally produced by reacting alcohols with two or more reactive hydroxyl (eOH) groups per molecule (diols, triols, polyols) with isocyanates. The environmental concerns of an isocyanates (R-N=C=O) liquid-phase process—which applies chlorobenzene and carbonyl chloride—has led to the consideration of the new technology, which manufactures both polyols and isocyanates from CO<sub>2</sub> via the production of hydroxyurethane from cyclic carbonate primary amine. This results in the manufacture of environmentally friendly non-isocyanate polyurethanes (Eq. 4).<sup>9,10</sup>

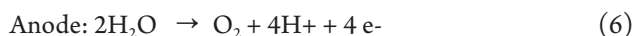


**Polycarbonates.** Polycarbonates constitute another group of CO<sub>2</sub>-based polymers. Among them, aliphatic polycarbonates can be directly produced by reacting epoxides with CO<sub>2</sub>. In addition, aromatic polycarbonates based on bisphenol A (BPA) can be produced by reacting an epoxide with CO<sub>2</sub> to produce an intermediate that is then polymerized.

Modern technologies of polycarbonate production plants apply CO<sub>2</sub> byproduct from ethylene oxidation to epoxide, leading to CO<sub>2</sub> reduction. Also, alternating polycarbonates can be derived from the reaction between an epoxide and CO<sub>2</sub>, which can be steered to polymeric organic carbonate, as depicted in **FIG. 2**. This is performed by suitable catalyst application.<sup>11</sup>

**Electrocatalysis applications in ethylene production.** Electrochemical reduction of CO<sub>2</sub> is an attractive process for ethylene production. Due to higher overpotentials, less selectivity and low stability, the process needs catalysts capable of selectively reducing CO<sub>2</sub> at lower overpotentials and with long run times. Various copper-based materials have been evaluated. The use of support materials like carbon nanostructures has been successfully employed both to enhance the selectivity and to increase the robustness of the catalyst.<sup>12</sup>

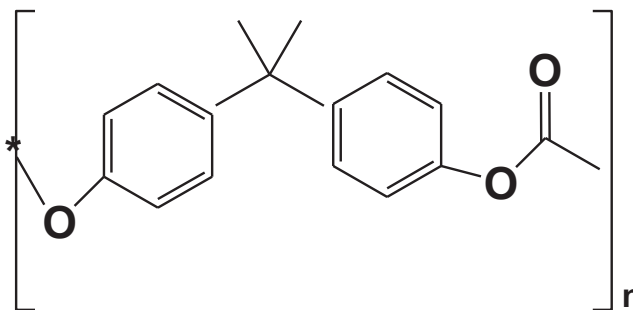
In this process, CO<sub>2</sub> is selectively converted to ethylene at the cathode with an accompanying evolution of oxygen gas at the anode in an aqueous solution. For process optimization, a renewable energy source is applied (Eq. 5 for the cathode, Eq. 6 for the anode):



The application of nanocarbons (carbon nanotube, graphene oxide, etc.) possessing high thermal conductivity, high theoretical specific surface area, unique carrier mobility and an sp<sup>2</sup>-hybridized carbon configuration have shown promotion to CO<sub>2</sub> photocatalysis applications, such as hydrocarbon synthesis.<sup>7</sup>

**Takeaways.** CO<sub>2</sub> is a sustainable resource of carbon that can partially replace oil and gas in many synthetic applications. Because it is recovered from industrial plants, it is considered a renewable, economical and green carbon feedstock.

CO<sub>2</sub> recycling can lead to a meaningful impact on CO<sub>2</sub> emis-



**FIG. 2.** Polymeric organic polycarbonate structure.

sions in the fields of fuels, chemicals and petrochemical materials. For the petrochemical industry, the emerging potential of chemical utilization of recycled CO<sub>2</sub> is organic carboxylation to polymeric carbonates. The purpose of its applications is due to the development of phosgene-free routes, which utilize CO<sub>2</sub> as a feedstock. In these cases, CO<sub>2</sub> serves as both carbon and oxygen sources, replacing CO for making acrylic acid and use as a mild oxidant. Additionally, its applications extend to environmental considerations since it is not toxic and can replace certain toxic building blocks, such as CO and phosgene, for producing methanol and polyurethane, respectively. **HP**

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## Save energy and reduce CO<sub>2</sub> emissions with closed-loop optimization of utilities networks

Oil and gas, petrochemical and chemical companies face the difficult challenge of maximizing profitability while achieving aggressive decarbonization objectives set for 2030 and beyond. The transition to a digitally powered business model is generally accepted across industries as companies adopt new processes, pursue new feedstocks and expand automation. Advanced process control (APC) and optimization technologies have long been used to help automate and optimize operations. More recent innovations have tackled strong process nonlinearities and multi-unit dynamic optimization of large process envelopes to better meet evolving, volatile market demands. Now, artificial intelligence (AI) and deep learning have further enhanced APC and optimization capabilities to help upstream and downstream companies achieve energy and carbon dioxide (CO<sub>2</sub>) reduction goals without significant capital investments. When applied to fuel gas, steam and hydrogen utility networks, APC and dynamic optimization technologies can have a tremendous impact in meeting an organization's operational and sustainability targets. This article explores why this is so important and how to achieve beneficial results with a utility network.

**Transitioning to a new business model.** Oil and gas, petrochemical and chemical companies are focused on tackling the dual challenge to meet the growing demand for resources from a growing population with increasing standards of living, while also addressing sustainability goals. To do so, these companies are transitioning to a new sustainable business model. This typically involves rebalancing their production portfolio and

investment areas, focusing on new feedstocks, new products, new energy sources and new process technologies. A digitalization journey framework leveraging new technologies like AI and deep learning can help with this transition. This journey is different from one organization to the next, with each being at a different digital maturity level. However, sustainability is always at the forefront of the transition and the new business model.

In fact, most companies have established aggressive sustainability targets for 2030, and particularly for CO<sub>2</sub> emissions reduction, with the European Union (EU) leading the way, setting a goal of 55% reduction from 1990 levels with full decarbonization to be achieved by 2050.

The global pandemic added more challenges and squeezed corporate margins, accelerating this transition process. Last year we witnessed high volatility in supply/demand and in energy costs, which has recently tripled in some regions. Extremely high CO<sub>2</sub> costs are prevalent in areas where a CO<sub>2</sub> trading and permit system is in place, such as the EU's Emissions Trading System (ETS).

A well-performing, complex 200,000-bpd European refinery that emits 1.5 MMtpy of CO<sub>2</sub> may need to buy around 200,000 tpy of CO<sub>2</sub> permits now worth around \$18 MM/yr, given current CO<sub>2</sub> prices of \$90/t—carbon pricing is based on cost in November/December 2021. Free allowances are forecast to be reduced each year and permit costs are likely to increase even more. This creates a sense of urgency to reduce energy and CO<sub>2</sub> costs to stay competitive, achieve sustainability goals or simply survive, as CO<sub>2</sub> costs may even move margins from positive to negative.

Owners and operators are planning significant capital expenditure (CAPEX) investments to achieve decarbonization targets set for 2030 and beyond. Examples of key investment areas include carbon capture, electrification, green/blue hydrogen, cogeneration and fuels-to-chemicals. These CAPEX investments are strategic, mid-to-long term and will require significant upfront investment with a high CO<sub>2</sub> abatement cost to achieve the targets. It is expected that these investments could help reduce carbon emissions by approximately 30%–35%.

An additional 20%–25% in carbon reduction is possible with more tactical investments to increase process efficiency. These would generally be less costly, low hanging fruit improvements that would not require executive level approval. There would be a negative CO<sub>2</sub> abatement cost since CO<sub>2</sub> reduction is typically accompanied by energy consumption reduction, making this secondary approach an attractive complement to longer-term, more strategic CAPEX investments.

### Process efficiency improvements.

APC and optimization technologies have been utilized in the process industries for several decades to enable improved process efficiency. Focusing first on large complex units and then secondary units, and more recently with large multi-unit envelopes in scope, like the entire middle distillates circuit in a refinery or a full ethylene plant in petrochemicals, optimized dynamically minute by minute. Optimization objectives have generally been in relation to increased capacity or yields, greater quality control or reduced giveaway, and—to a lesser extent—energy savings. Priorities for most providers

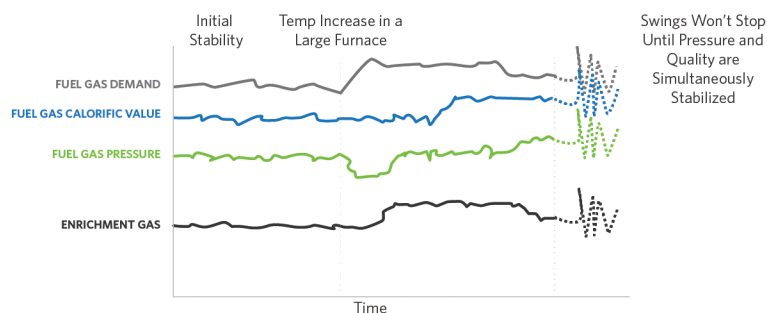


FIG. 1. Fuel gas network pressure and quality interaction.

have shifted dramatically during the past 2 yr, with energy reduction, production cost reduction and increased agility becoming the top focus areas.

APC and optimization technologies are the most cost-effective option to improve process efficiency and support the decarbonization process. It is worth noting that with carbon prices continuing to increase, the value from CO<sub>2</sub> reduction becomes as significant a benefit as energy reduction savings.

There are a multitude of efficiency improvement opportunities available to refiners. These include:

- Increasing furnace efficiency
- Minimizing distillation columns' pressure against actual unit constraints
- Minimizing load and optimizing the purification level of distillation columns
- Minimizing quality giveaways to avoid excess energy consumption
- Minimizing circulation, reprocessing and recycling
- Making the right product recovery/energy consumption tradeoffs
- Maximizing heat/cold recovery
- Integrating multiple units and managing heat balances
- Balancing demand/supply to avoid losses (e.g., hydrogen, steam)
- Minimizing downgrades (e.g., steam, fuels, hydrogen, products)
- Maximizing equipment efficiency
- Optimizing utilities networks: fuels, hydrogen and steam.

APC is now capable of solving difficult nonlinear problems. In addition, it enables an adaptive workflow to maximize model accuracy, lets users make changes to economic objectives on the fly, and embeds AI and deep learning capabilities to leverage a wealth of histori-

cal data to obtain models and solve complex problems—for instance, inferring highly nonlinear qualities that depend on the type of run, feedstock qualities or grade to be produced.

With dynamic, self-adapting optimization capabilities that automatically align models and the process, a true overall optimum can be achieved across a large process scope.

These capabilities and technology enhancements enable users to solve complex problems, such as utilities networks, which were previously difficult to solve.

The rest of this article focuses on optimization strategies, which represent tremendous energy- and CO<sub>2</sub>-saving opportunities in the three primary site networks: fuel gas, hydrogen and steam.

**Fuel gas network optimization.** For many facilities, fuel gas network optimization can be a significant issue that must be addressed. The following are some of the most common challenges:

- Fuel gas network pressure (volume) and quality interact heavily
- Volume balance models are integrating processes as pressure builds up as a ramp
- Quality models are nonlinear, and gains may even change from positive to negative or vice versa
- Various makeup gases are typically available, and their quality may change over time
- Additional makeup gas reduces the effect on overall network quality due to nonlinearities from mixing
- Inherent instability due to disturbances continuously entering the system.

The quality of gas streams entering the network varies continuously. If en-

richment gas with a high heating value is added to control the pressure, the heating value of the fuel gas increases. The furnaces will then have to cut their consumption, which will upset the volume balance, and the enrichment gases will also be cut back.

This behavior keeps repeating, leading to a self-propagating cycle impacting the performance of fuel gas users across the whole site. Fuel gas instability can result in scenarios such as units cutting back load, increasing load to blowdown networks and gas recovery compressors, and flaring events.

This behavior, illustrated in FIG. 1, can cause excessive energy consumption and CO<sub>2</sub> emissions. With integrating processes like volume balance models, which exhibit strong nonlinearity, model gains can flip their sign (i.e., go from positive to negative or vice versa) as the quality effect of the enrichment gas depends on the current network's calorific value.

Multiple enrichment gases may be available to control pressure, and each gas can increase or decrease the network calorific value. The impact may change over time depending on current calorific values of both gas and the network. Adding more makeup gas changes the effect as the gap between the two qualities changes.

FIG. 2 illustrates the potential effects of these nonlinearities. For instance, the same changes to the same enrichment gas may have very different effects on the network's calorific value. Addressing these challenges is possible by adopting a nonlinear adaptive process control solution<sup>a</sup> to solve highly nonlinear and interactive problems and reach desired outcomes. The adaptive process control solution<sup>a</sup> lets users easily revise economic objectives to continuously minimize the overall cost of the streams entering the fuel gas network.

The following are some other key benefits of using such a nonlinear adaptive process control solution:

- Simultaneously control both fuel gas pressure and quality (calorific value), stabilizing operations throughout the site
- Minimize/avoid flaring
- Minimize blowdown discharge and subsequently gas recovery compressor power consumption
- Improve furnace efficiency through consistent and stable firing, which enables further reduction in excess air



- Tackle every furnace throughout the refinery to ensure proper control over combustion and oxygen concentration (e.g., for a furnace with 80% efficiency, a 5% reduction in oxygen from 3.5% to 3.33% can result in roughly a 0.3% increase in efficiency)
- Control emissions in closed loop within the APC applications (not simply monitoring emissions) wherever it makes sense to do so
- Reduce the overall cost of fuels entering the fuel gas network or being directly fired, whenever flexibility to use different types of fuel exists, and improve overall profitability
- Significantly reduce CO<sub>2</sub> emissions, considering that around 2.78 t of CO<sub>2</sub> are emitted for each ton of fuel gas.

The 200,000-bpd refinery in our example can reduce fuel gas flaring and blowdown by more than 50%, improving overall combustion efficiency and process unit performance, reducing CO<sub>2</sub> emissions by 19,000 tpy and achieving savings of \$4.6 MM/yr.

Typical available control handles include:

- Natural gas entry points
- LPG vaporizers
- Fuel oil/fuel gas balancing in double firing boilers/furnaces
- Streams manipulated to support fuel gas network pressure (e.g., propane, LPG)
- Fuel gas exchange streams to/from various headers and sections.

Pre-requirements are usually minimal, and a calorific value analyzer may be required only if accurate and sufficiently robust inferentials cannot be built based on available density analyzers and lab analysis. Nonlinear inferencing capabilities of proprietary software<sup>b</sup> can be leveraged to build such inferentials.

**FIGS. 3 and 4** show fuel gas header pressure and calorific value before and after deploying the APC solution.

**Hydrogen network optimization.** Hydrogen network optimization is another significant opportunity to improve overall process efficiency and support decarbonization objectives.

Most refineries are either hydrogen or desulphurization capacity limited (some

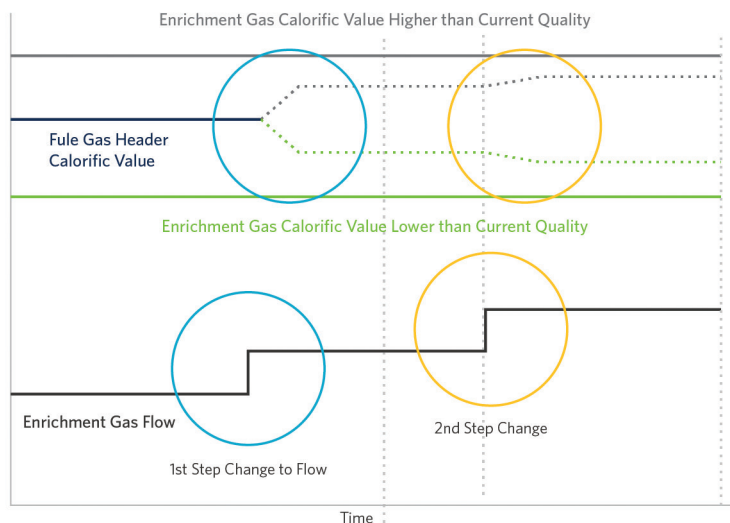
are both). In all cases, hydrogen must be produced and used optimally. A refiner's planning/scheduling department typically provides guidance on hydrogen producers'/consumers' load and what to do in case of excess or the lack of hydrogen, but coordination remains infrequent, manual and sub-optimal.

Due to the high cost of natural gas, the cost of producing hydrogen is expensive (presently topping \$3,000/t in some sites for pure hydrogen, depending on how hydrogen is produced). Moreover, producing 1 t of hydrogen in a steam reformer results in approximately 10 t of CO<sub>2</sub>, having significant impact on site emissions.

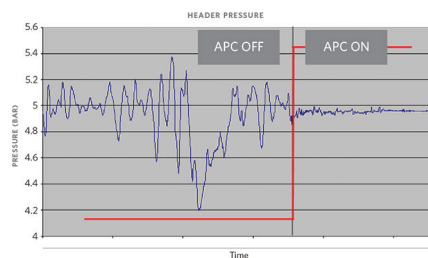
It is imperative to avoid wasting hydrogen to fuel gas—every kilogram counts since a reduction of just 200 kg/hr of hydrogen results in overall savings of \$2 MM/yr in energy and CO<sub>2</sub> benefits.

Besides the economic loss, hydrogen discharges to the fuel gas network disturb overall operations given that the hydrogen calorific value is 2 times–3 times that of a typical fuel gas. There is certainly the need to dynamically coordinate hydrogen producing and consuming units, which are often under different operators' responsibilities. Some challenges and peculiarities must be considered, including:

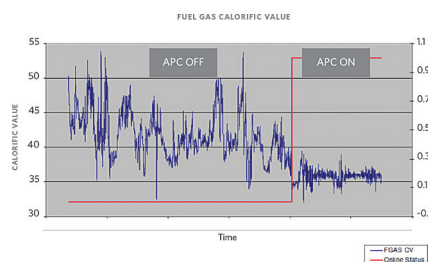
- The hydrogen network can be very complex, with multiple headers at different pressures and purities, up to 4–6 suppliers (reformers, steam reformers, partial oxidation units, gasifiers, etc.) and up to 10–15 consumers



**FIG. 2.** Fuel gas networks' nonlinearities.



**FIG. 3.** Fuel gas pressure before and after deploying the APC solution.



**FIG. 4.** Fuel gas calorific value before and after deploying the APC solution.

(hydrocrackers, hydrotreaters, desulphurization units, tail gas treaters, isomerization units, etc.) and compressors, pressure swing adsorption (PSA)/membranes, or other purification units.

- Hydrogen headers usually have different pressures and qualities and are interconnected through valves or compressors.
- Disturbances in one of the suppliers or consumers can impact the entire system with variations



- in hydrogen quality and pressure.
- Optimum dynamic operational changes. Constraints may show up in different units and scenarios may change significantly based on costs and the availability of feeds, conversion/desulphurization units' margins and market conditions.
- There are nonlinearities to be addressed and tradeoffs to be managed like purities, catalyst lifecycles, losses and recoveries based on required hydrogen purities and associated consumptions.
- There is sometimes a lack of ownership of coordination of multiple producers and consumers.

Hydrogen consumption is forecast to increase in the short- to mid-term due to multiple reasons, such as tighter desulphurization targets being enforced and

the need to co-process more renewable feedstocks in hydrotreaters due to local regulations. For example, a 3% vegetable oil coprocessing could require 20% more hydrogen.

Hydrogen networks interact with both gasoline and middle distillates' circuits. Within a gasoline circuit, tradeoffs may exist between hydrogen production and gasoline production requirements. Within a middle distillates circuit, the tradeoffs are between unit loads, feed blending (e.g., vegetable oils, cracked feeds or vacuum gasoils) and hydrogen availability.

If such tradeoffs are identified, the most practical way to address them is to integrate the hydrogen network optimizer with the production circuit optimizer(s).

With a scope encompassing production circuits (targeting reduction of qual-

ity giveaways), additional benefits in terms of energy and CO<sub>2</sub> savings can be achieved, as any giveaway results in additional energy consumption.

A hydrogen network can be effectively optimized by leveraging dynamic optimization technology<sup>c</sup> in combination with an adaptive process control solution.<sup>a</sup> This addresses nonlinearities and coordinates multiple units dynamically by relying on an ever-green adaptive APC layer to reach desired objectives.

Such an application typically enables users to:

- Balance production of and demand for hydrogen, ensuring it is optimally distributed
- Optimize steam reformer operations and conversion
- Minimize hydrogen discharge to fuel gas network and blowdown
- Reduce power consumption in gas recovery compressor(s), if any
- Minimize hydrogen production costs whenever this flexibility exists
- Increase profitability of conversion and desulfurization units
- Stabilize hydrogen header pressures and purities
- Optimize hydrogen network purities
- Significantly reduce CO<sub>2</sub> emissions.

Assuming the 200,000-bpd European refinery discharges 500 kg/hr of hydrogen to fuel gas, it can reduce the loss by at least 50%, reduce CO<sub>2</sub> emissions by 18,000 tpy and achieve savings of approximately \$4 MM/yr. Additional benefits can be realized due to reduced hydrogen production costs and more profits coming from hydrogen users.

It is not uncommon for sites to discharge approximately 1 t/hr of hydrogen or more on average to the fuel gas network, as shown in FIG. 5.

The following are some typical available control handles:

- Steam reformer(s) hydrogen production
- Reformer(s) severities (when possible and not fixed on gasoline balance)
- Bypasses between headers of different purities
- Purge rates from consuming units

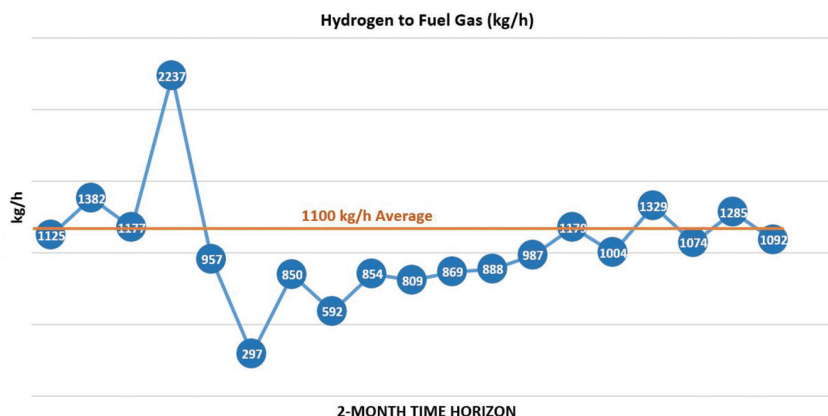


FIG. 5. Approximately 1 tph of hydrogen discharged to fuel gas over 2 mos for a 200,000-bpd refinery.

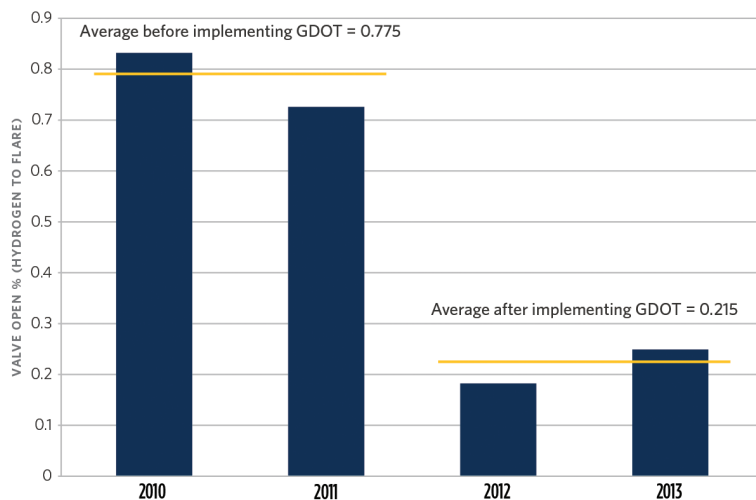


FIG. 6. Hydrogen discharged to the flare 2 yr before and after the dynamic optimization technology<sup>c</sup> was implemented in a 220,000-bpd refinery. Source: A. Porcel and K. Kahlgren, "Dynamic optimization moves into mainstream," ERTC, November 2018.

- PSA and membrane operation
- Hydrocracker (or another selected unit) load to balance hydrogen consumption.

Pre-requirements are usually minimal. Unlike the applications on production circuits, a hydrogen network optimizer does not require an APC layer on most of the units in the envelope. If the load (throughput) of a process unit is to be optimized, then an APC layer is required on the unit.

FIG. 6 illustrates four consecutive years of hydrogen losses to flare, two years before and after implementation of dynamic optimization technology<sup>6</sup>, with a minimum 70% reduction in losses.

**Steam network optimization.** Steam production systems must satisfy the demand coming from process units at the lowest possible cost. These networks can be very complex with multiple headers, boilers, gas turbines and heat recovery steam generators (HRSGs), as well as different types of turbines and turbogenerators.

FIG. 7 shows a complex network in an ethylene plant with seven headers, two boilers, six turbines, numerous turbomachines, hundreds of users and more than 10 steam pressure controllers. Of course, optimizing this network is quite challenging. Header pressures for high-, medium- and low-pressure steam must be controlled tightly, and the overall efficiency must be maximized by properly addressing nonlinearity, which is dependent on load distribution and equipment availability.

Another issue to consider is that steam networks are continuously affected by disturbances from process units. Within the network, header pressures interact between themselves. Moreover, there are constraints on power import/export and a need to balance steam/power production. Cost variability may impact the optimal operating point dynamically, as often as daily or even more frequently.

Steam letdowns and venting must be minimized or avoided, as they can result in excessive fuels consumption and higher CO<sub>2</sub> emissions/t of steam produced. Consumptions and related emissions strongly depend on the steam production infrastructure, efficiencies and fuels used. A reasonable estimate is that 12-t

of high-pressure steam consumes 1 t of fuel gas, and each ton of fuel gas emits 2.78 t of CO<sub>2</sub>. Therefore, 0.23 t of CO<sub>2</sub>

gets in mind. The following are several examples of units to consider for APC applications:

**Recent advancements in APC and optimization technologies provide strong options for oil and gas and chemical companies faced with the challenge of achieving energy efficiency and reducing carbon emissions.**

are emitted for each ton of high-pressure steam produced.

Any amount of steam lost or downgraded to a lower pressure level without producing energy impacts the site's energy bill and CO<sub>2</sub> balance. It is necessary to dynamically coordinate energy producers and consumers, often under different operators' responsibility or even operated in separate control rooms.

A steam network can be effectively optimized by leveraging the nonlinear adaptive process control solution<sup>3</sup>, typically in combination with an optimizer that sets targets for the APC layer considering the overall utilities system. This must be considered, given that the steam and fuel networks interact, and a single overall optimum exists. Such an application typically enables users to:

- Stabilize high-, medium- and low-pressure steam header pressures by properly managing boiler/turbine loads and turbine spills
- Maximize boiler efficiency, while guaranteeing proper high-pressure control
- Optimize boiler(s) combustion
- Maximize overall efficiency by optimally distributing loads across equipment.
- Continuously minimize direct letdowns (and vents if any) if this is the most economical solution
- Significantly reduce CO<sub>2</sub> emissions.

In addition, every steam user must be evaluated to ensure that energy targets are actively pushed by local APC applications. For example, columns must be operated at their minimum pressure against process constraints and not at pressure limits set by an operator. Also, live steam constraints of columns or fractionators must be active (e.g., flash point or hydrogen limit instead of with steam/flow ratios).

Every APC application objective should be revised with the energy tar-

- Distillation columns
- Amine regenerators
- Sour water strippers
- Fractionators live steam
- Side strippers
- Compressors/steam turbine drives.

Multiple opportunities exist in using the steam network. For example, FIG. 8 shows that more than 10 t/hr of high-pressure steam is downgraded to medium-pressure header during normal operations. Some typical available control handles include the following:

- Boiler/turbine/HRSG loads
- Turbine spills

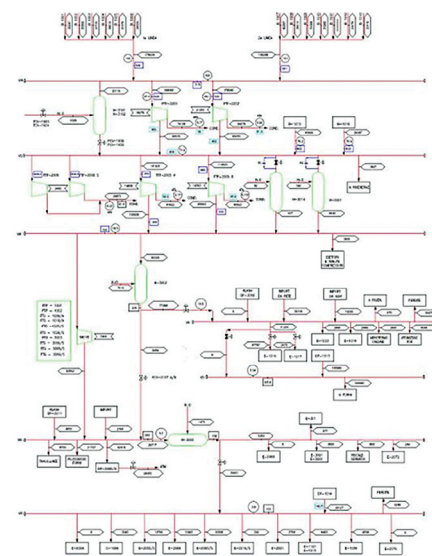


FIG. 7. Ethylene cracker steam network.

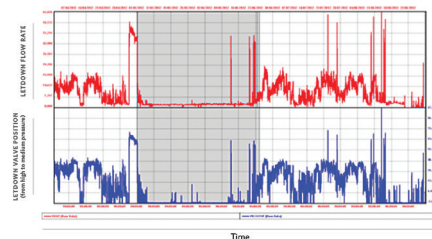
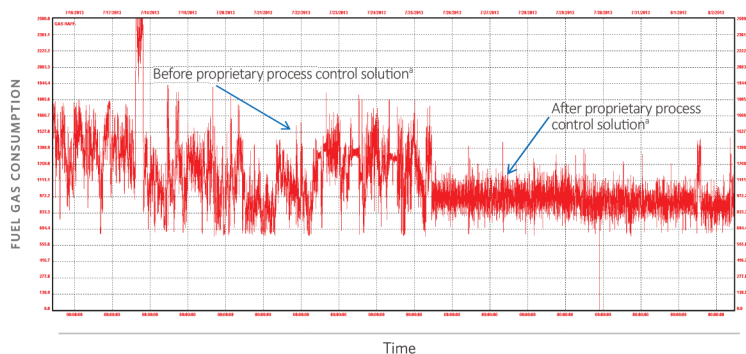
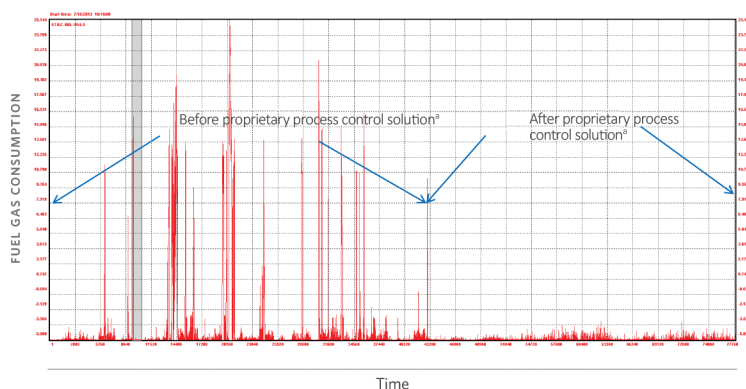


FIG. 8. Letdown flowrate and valve position.

**TABLE 1.** Optimization benefits for the three networks

Network	Energy, \$MM/yr	CO <sub>2</sub> , thousand tpy
Fuel gas	4.6	19
Hydrogen	4.1	18
Steam	2.9	12
<b>Total</b>	<b>11.6</b>	<b>49</b>

**FIG. 9.** Fuel gas consumption before and after optimization. Source: G. Ruggeri, S. Chillemi, J. C. Duarte and S. Dhaliwal, “Balancing steam network production and demand improves power generation,” AspenTech OPTIMIZE 2015.**FIG. 10.** Letdown before and after optimization. Source: G. Ruggeri, S. Chillemi, J. C. Duarte and S. Dhaliwal, “Balancing steam network production and demand improves power generation,” AspenTech OPTIMIZE 2015.

- Carbon monoxide (CO) boiler load (if present)
- Other local steam production equipment and medium-/low-pressure streams to the network
- Boiler combustion handles
- Flexibilities in header pressure control
- Steam exchange streams.

Significant benefits can be achieved (FIGS. 9 and 10). Both figures show a reduction in fuel gas consumption and letdown before and after optimization. Using the same refinery example, savings of \$2.9 MM/yr can be achieved and up to

12,000 tpy of CO<sub>2</sub> saved through steam network optimization.

**Takeaway.** In these volatile times, recent advancements in APC and optimization technologies provide strong options for oil and gas and chemical companies faced with the dual challenge of achieving energy efficiency and reducing carbon emissions. With no CAPEX investment needed, these solutions can quickly deliver significant process efficiency improvements and a negative CO<sub>2</sub> abatement cost (i.e., a net profit).

Utilities networks in refineries, petrochemical and chemical sites present

clear optimization opportunities to save energy and reduce CO<sub>2</sub> emissions, supporting widely adopted decarbonization programs across the process industry.

Considering energy and CO<sub>2</sub> reduction benefits for the three networks, TABLE 1 shows optimization achievements for the 200,000-bpd European refinery example used throughout this article. CO<sub>2</sub> emissions reduction in this case represents 3.3% of the overall refinery emissions, with a value of more than \$4 MM/yr at the current price for CO<sub>2</sub> in Europe of \$90/t. Note that the 49,000 tpy of CO<sub>2</sub> in column three of TABLE 1 is approximately 25% of the CO<sub>2</sub> permits that the 200,000-bpd European refinery example would need to buy every year. Additional benefits can be obtained from process units, primarily from capacity and yield increases. An increase in yields generally results in additional energy savings due to a reduction in costly quality giveaway.

These results can be achieved by leveraging recent APC and optimization technology enhancements that enable users to efficiently address problems that were previously difficult to solve. These enhancements include:

- Adaptive process control to maintain ever-green models
- Full nonlinear control
- AI to identify models and build inferred properties to cope with different run modes and nonlinearities
- Flexibility to change optimization strategy rapidly
- Self-adapting dynamic optimization for multi-unit optimization of large envelopes. **HP**

#### NOTES

<sup>a</sup> Aspen DMC3™

<sup>b</sup> Aspen Deep Learning IQ

<sup>c</sup> Aspen GDOT™



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## CO<sub>2</sub> compressor technology for a decarbonized energy economy

Due to the potential of hydrogen (H<sub>2</sub>) in the context of developing a decarbonized energy infrastructure, technologies for efficiently producing, transporting, storing and utilizing it have attracted significant investment.

Of the three H<sub>2</sub> production processes commonly used on an industrial scale (steam reforming, partial oxidation gasification and electrolysis), two require hydrocarbons for feedstock and emit significant amounts of carbon dioxide (CO<sub>2</sub>) as a byproduct—the outlier is electrolysis, which requires only water and an electric power source and can be powered by renewable energy. Steam reforming and partial oxidation gasification, by contrast, are complex chemical processes that convert a fossil fuel (natural gas or coal, respectively) into H<sub>2</sub>, carbon monoxide (CO) and other compounds.

Due to the low cost of fossil fuels and corresponding plant process equipment, 98% or more of H<sub>2</sub> now produced is derived using one of these two methods. Converting natural gas to H<sub>2</sub> is a proven, relatively inexpensive process, particularly in North America where natural gas is abundant; even were gas prices to rise, the conversion of coal to H<sub>2</sub> would still be both commercially viable and less expensive than electrolysis. Therefore, the most realistic path to decarbonization involves the sequestration of CO<sub>2</sub> emitted during the H<sub>2</sub> production process, rather than its elimination. As such, three important gas streams must be managed, even in a decarbonized economy:

1. The production of natural gas, followed by its transportation to a site where it can be converted into H<sub>2</sub>

2. The transport of H<sub>2</sub> to its end-use site, either an industrial facility or a power plant
3. The transport of CO<sub>2</sub> to an appropriate geological sequestration and end-storage site.

These gas streams will require substantial compression. As the complexities of both natural gas and H<sub>2</sub> compression have been extensively covered elsewhere, this article is chiefly concerned with solutions for the compression and transport of CO<sub>2</sub>. While CO<sub>2</sub> compression has been successfully undertaken for many years as part of acid/sour gas injection and enhanced oil recovery projects, the scale-up required for carbon separation and sequestration in a decarbonized H<sub>2</sub> scenario would challenge even technologies now considered state-of-the-art. Because of this, a need exists for new CO<sub>2</sub> compression applications for separation, transport and storage injection.

**CO<sub>2</sub> compression: An overview.** The pressure of CO<sub>2</sub> gas separated from the newly produced H<sub>2</sub> is strongly dependent on the type of separation process utilized: as such, it can vary from only slightly above atmospheric pressure to several hundred psi. Additionally, significant uncertainty surrounds geological formation injection pressure, since it depends strongly on the type of formation and its drilled depth of injection.

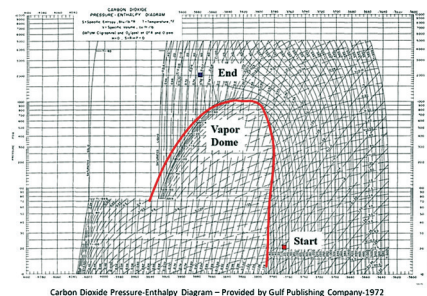


FIG. 1. Compression start and endpoint on CO<sub>2</sub> pressure-enthalpy diagram.

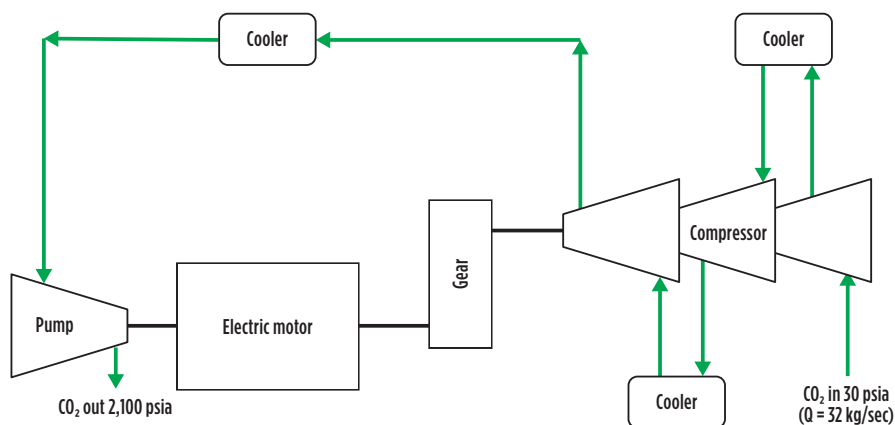


FIG. 2. Intercooled centrifugal barrel compressor feeding a dense phase pump.



The generally accepted rule, however, is that for each km of depth of injection, ~1,150 psi of gas pressure is required. Since many of the geological formations presently under consideration for CO<sub>2</sub> storage are relatively shallow, injection pressures below 2,000 psi should be expected to occur frequently. A typical carbon separation and storage pressure application requires CO<sub>2</sub> to be compressed from below 50 psia to above 2,100 psia, as shown in FIG. 1.

Many viable thermodynamic path options, including refrigeration and liquid pumping, near-isothermal, and high-pressure ratio compression, exist to move this compression process from its start to its endpoint. Put differently, the available options are to compress the CO<sub>2</sub> and remain in the gas state on the right side of the vapor dome, refrigerate the CO<sub>2</sub> and pump it in the liquid state on the left side of the dome, or utilize some combination of these methods.

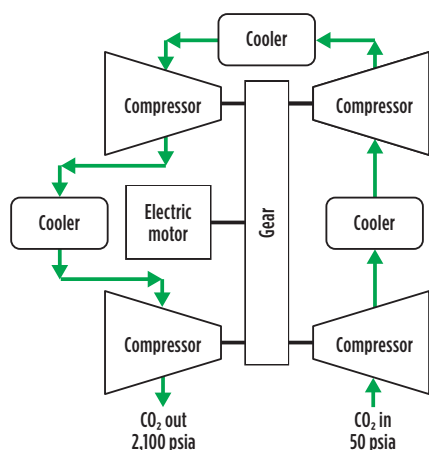


FIG. 3. Integrally geared compressor with interstage cooling.

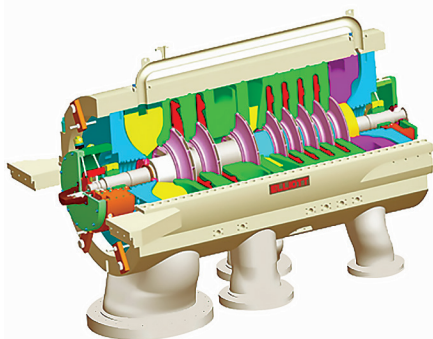


FIG. 4. An 8-impeller-stage, barrel-type, centrifugal compressor with multiple nozzles for intercooling or side streams.

**CO<sub>2</sub> sequestration and storage.** For most power plant carbon capture and sequestration applications, the following new compression duties are required:

1. Pipeline header injection and recompression transport
2. Injection into geological storage reservoirs for sequestration
3. Separation processes (membrane, thermal or chemical)
4. Power plant cycle compression.

According to industry convention, CO<sub>2</sub> as a supercritical (dense phase) fluid above 2,100 psi should be transported in pipelines. At 2,100 psi, CO<sub>2</sub> is well above its critical point and will be supercritical at almost all ambient temperatures. Fluids in a dense phase share some physical properties of liquids, such as a very low compressibility; they also share some physical properties of gases and will expand in space to fill voids. The advantage of transporting CO<sub>2</sub> at supercritical pressures, therefore, is that its density does not change much with pressure: from a thermodynamic perspective it is essentially pumped rather than compressed. This significantly reduces the power demand for the pumping stations along a CO<sub>2</sub> pipeline.

There are two disadvantages, however: the added injection compression ratio required at the pipeline header station and the significantly higher material costs when building a pipeline designed for a maximum allowable operating pressure above 2,100 psi. Since the CO<sub>2</sub> available from separation is at low, near-atmospheric pressures (< 100 psi), the pipeline header station must always use a compressor; for a 2,100-psi CO<sub>2</sub> pipeline, a high-pressure ratio header compressor with many intercooled stages will be needed to handle the significant volume reduction. In such a case, however, beyond the header station the gas is simply pumped.

Fortunately, transport at 2,100 psi is

not required for all applications: the actual transport pressure of CO<sub>2</sub> depends on the separation process outlet starting pressure, the distance the CO<sub>2</sub> must be transported and the geological sequestration injection pressure (which is often well below 2,100 psi). If a lower-pressure CO<sub>2</sub> pipeline is utilized, conventional compressors are preferred for the header station and for recompression along the line. The transport pressure is selectable depending on the carbon sequestration application; it is not always advantageous to go with supercritical CO<sub>2</sub>.

Purely from a compression stage thermodynamic perspective, CO<sub>2</sub> is a heavy gas but relatively easy to compress. That ease notwithstanding, CO<sub>2</sub> presents several technical challenges that must be addressed to make its compression or pumping process efficient and reliable. These include:

- Most equations of state for CO<sub>2</sub> are still inaccurate at high pressures and temperatures.
- CO<sub>2</sub> is a heavy gas, resulting in amplified rotor dynamic and impeller-dynamic forces.
- CO<sub>2</sub> has a strong thermodynamic path dependence and multi-phase behavior.
- CO<sub>2</sub> forms carbonic acid in the presence of water, which then drives corrosion.
- CO<sub>2</sub> is soluble in elastomeric materials, which can lead to rapid decompression failures.
- When rapidly expanded, CO<sub>2</sub> quickly forms liquids and dry ice, which can be a problem at the shaft seals.
- CO<sub>2</sub> has a low sonic speed, which results in higher shock losses and a reduced operating range.
- CO<sub>2</sub> selectively leeches certain elements from common metals and has a very low viscosity at high pressures.

All of these represent manageable, if complex, engineering and design challenges.

#### Compression and pumping options.

CO<sub>2</sub> has a high pressure ratio per compressor impeller stage. Because of this, it also has a significant specific volume decrease with pressure along with a very high heat of compression. This means that CO<sub>2</sub> heats up when compressed and requires stage intercooling to maintain

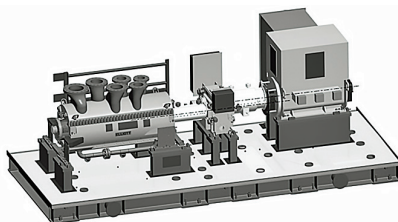


FIG. 5. A multi-stage, horizontally split compressor with nozzles for two intercoolers driven by an electric motor through a gearbox.

the gas temperature at reasonable levels so as not to damage the compressor seals and bearings. Furthermore, because of its rapid density change with pressure, a significant flow volume reduction requires a wide range of aerodynamic high-to-low flow compression stages.

The following types of compressors are typically considered for high-pressure-ratio carbon sequestration applications:

- Reciprocating
- Screw
- Centrifugal barrel
- Centrifugal horizontally split
- Integrally geared
- Hybrid centrifugal with dense phase pump.

Since both reciprocating and screw compressors are severely flow limited, in practice they cannot be used for large-scale carbon sequestration applications; the other options all rely on proven centrifugal compressor or pump impellers and differ primarily in their layouts and stage arrangements. The best configuration for the application type under discussion is either an intercooled, barrel,

straight-through centrifugal compressor with a dense phase pump (FIG. 2) or an integrally geared intercooled compressor (FIG. 3). Both arrangements require seven to eight compression or pumping stages, with intercoolers between them, to meet the specified compression ratio (for simplicity's sake, the schematics shown do not include all stages). Industry opinions vary as to which is the better selection: both arrangements have pros and cons depending on operating conditions and range, application-specific standards, plant type, maintenance expectations and service cycle.

**Compressor designs.** The two designs discussed above represent the most promising options, not the only ones. Several other machinery solutions for compression and pumping of CO<sub>2</sub> are commercially available, such as the multi-stage barrel centrifugal compressor shown in FIG. 4 or the horizontally split centrifugal compressor in FIG. 5. In both cases, two casing section intercoolers and one discharge cooler are required to avoid over-

heating and achieve efficient CO<sub>2</sub> compression; typical operating conditions for these machines range from < 50 psia (for suction pressures) to > 1,100 psia (for discharge pressures). At 1,100 psia, the compressor discharge gas will be in the supercritical state, meaning that after cooling the CO<sub>2</sub> can be fed directly into the dense phase pump for higher-pressure pipeline transport or storage injection. Although the technical challenges of CO<sub>2</sub> compression are often application-specific and must be individually addressed for new carbon sequestration technologies, a wide toolkit is available for further development, as necessary. **HP**



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## Assessment protocol for nozzle loads on pressure vessels

From a historical perspective, the traditional approach to deal with “unknown magnitude of nozzle loads” can be summarized here.

In EN 13445-3 (EU)<sup>1</sup> clause 16.4.6.3 and 16.5.6.3, if the ratio  $\Phi_p = 1$ , then the other ratios,  $\Phi_z$  and  $\Phi_B$ , must be zero for the interaction requirements to be met, although there is some provision in equations 16.4-15 and 16.5-15 for the other ratios to be slightly greater than zero. The equivalent clauses, as indicated in PD 5500 (UK),<sup>2</sup> are, respectively, G.2.8.2.4 and G.2.8.3.4, and the equations G.2.8-13 and G.2.8-39.

This means that for the initial design, some provision must be made for nozzle loads that are not yet known. This has always been the case, and many companies have produced their own data tables of nozzle loads that are used for the initial design. The piping stress analysts then know that they must maintain the calculated nozzle loads to less than the tabulated values and design the piping accordingly.

In the absence of tabulated nozzle loads for a particular job, vessel designers must use their engineering judgement and experience to assess whether the loads are likely to be small (moderate temperatures and well-designed piping with plenty of flexibility), or large (high temperatures, compact layout with little piping flexibility) and then design the nozzles for appropriate, estimated loads. The designer may choose to use tabulated loads from another similar project.

Some degree of overdesign always exists in any pressure vessel, but it is not usually practical to wait until the piping design has been completed before beginning to design the vessels. If the vessels are designed before the nozzle loads are known, it is often cheaper to overdesign the nozzles rather than try and modify the design at a later stage after fabrication has begun.

Where ASME BPVC Section VIII Division 1<sup>3</sup> is the prevailing design code, the commonly used approach to assess nozzle loading is using WRC Bulletins 107<sup>4</sup>, 537<sup>5</sup> and 297<sup>6</sup>—with the understanding that the internal pressure load must also be considered, which is not an integral part of the WRC bulletins.

To support the engineer involved in the design of pressure vessels, a protocol has been developed that enables the engineer to gain insight into the individually permissible loads on a flanged nozzle configuration of a pressure vessel. This protocol can be applied to recognized pressure vessel codes and/or standards including: EN 13445 (EU)<sup>1</sup>, PD 5500 (UK)<sup>2</sup> and

ASME BPVC Section VIII-Division 1(U.S.)<sup>3</sup>. The involvement of the piping stress analyst is limited to evaluating the piping reactions from the pipe stress analysis to the allowable nozzle loads determined by the vessel design engineer, considering only internal pressure.

It has been noted that in the methodologies contained in both EN 13445-3 (clauses 16.4.6 and 16.5.6) and PD 5500 (clauses G.2.8.2 and G.2.8.3), no external loads can be allowed by the nozzle exerted piping reactions if  $\Phi_p = P_{\text{design}}/MAWP = 1$ .

However, this implies that only external loads are allowed if  $\Phi_p < 1$ , which means that a certain amount of “overdesign” must be created compared to exclusively incorporating internal pressure loading in the nozzle design. ANNEX V of EN 13445-3 (amendment A8: 2019)<sup>7</sup> states that a buffer should be considered for unknown nozzle loads that relate to the opening design. Literature<sup>8</sup> highlights the doubts that have arisen about this approach.

From this perspective, an alternative approach has been developed that is based on the fact that nozzles designed for internal pressure still have sufficient load-carrying capacity left to accommodate the piping reactions on the nozzle. The advantage of this approach lies in the fact that, in contrast to the traditional approach outlined, the permitted (individual) nozzle loads can already be determined during the initial pressure vessel design by the vessel design engineer and can be made available to the piping stress analyst. Obviously, this requires the necessary co-ordination between the two engineering disciplines. This innovative approach has proven itself in successful applications for many years in predominantly statically loaded pressure vessels.

**Determination of individually permissible loads.** The method described by the author<sup>9</sup>, which is based on Dekker and Bos<sup>10</sup>, was used to determine the individually permissible nozzle loads.

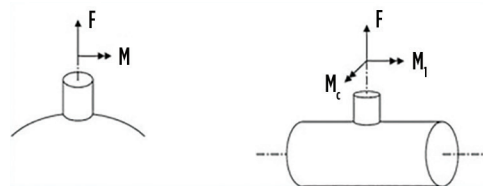


FIG. 1. Nozzle configurations and loadings.

**TABLE 1.** Applicable formulas for calculating the permissible nozzle loads

Maximum allowable individual loads Nozzles in cylindrical shells w/o reinforcing plate	Maximum allowable individual loads Nozzles in spherical shells w/o reinforcing plate	Maximum allowable individual loads Nozzle in cylindrical shells with reinforcing plate (Adjacent to nozzle neck)	Maximum allowable individual loads Nozzle in spherical shells with reinforcing plate (Adjacent to nozzle neck)
$F = \frac{\sigma}{6 C_{21}}$	$F = \frac{\sigma}{1.75 C_{21}}$	$F = \frac{\sigma}{6 C_{21}}$	$F = \frac{\sigma}{1.75 C_{21}}$
$M_l = \frac{\sigma}{1.5 C_{31}}$	$M = \frac{\sigma}{1.75 C_{31}}$	$M_l = \frac{\sigma}{1.5 C_{31}}$	$M = \frac{\sigma}{1.75 C_{31}}$
$M_c = \frac{\sigma}{1.15 C_{31} \times C_{41}}$		$M_c = \frac{\sigma}{1.15 C_{31} \times C_{41}}$	
<b>Auxiliary values</b>		<b>Auxiliary values</b>	
$C_{11} = \frac{(D_o - T)}{2T}$		$C_{11} = \frac{(D_o - (T + T_{pad}))}{2(T + T_{pad})}$	
$C_{21} = \frac{(C_{11})^{0.5}}{\pi \times T \times D_n}$		$C_{21} = \frac{(C_{11})^{0.5}}{\pi (T + T_{pad}) \times D_n}$	
$C_{31} = \frac{4(C_{11})^{0.5}}{\pi \times T \times (D_n)^2}$		$C_{31} = \frac{4(C_{11})^{0.5}}{\pi (T + T_{pad}) D_n^2}$	
$C_{41} = \left( \frac{D_n}{2T} \right)^{0.5}$		$C_{41} = \left( \frac{D_n}{2(T + T_{pad})} \right)^{0.5}$	
Maximum allowable individual loads Nozzles in cylindrical shells with reinforcing plate (At transition between vessel and reinforcing plate)	Maximum allowable individual loads Nozzles in spherical shells with reinforcing plate (At transition between vessel and reinforcing plate)	<b>Maximum allowable individual flange loads</b>	
$F = \frac{\sigma}{6 C_{22}}$	$F = \frac{\sigma}{1.75 C_{22}}$	$F = (P_r - P_d) \frac{\pi}{4} G^2$	
$M_l = \frac{\sigma}{1.5 C_{32}}$	$M = \frac{\sigma}{1.75 C_{32}}$	$M = (P_r - P_d) \frac{\pi}{16} G^2 \times C \times K_f$	
$M_c = \frac{\sigma}{1.15 C_{32} \times C_{42}}$		<b>Auxiliary value</b>	
<b>Auxiliary values</b>		$K_f = 1 + \frac{t^2 + (W - d_{bh}^*)^2}{2.6 t^2}$	
$C_{12} = \frac{(D_o - T)}{2T}$			
$C_{21} = \frac{(C_{12})^{0.5}}{\pi \times T \times D_{pad}}$			
$C_{32} = \frac{4(C_{12})^{0.5}}{\pi \times T \times (D_{pad})^2}$			
$C_{42} = \left( \frac{D_{pad}}{2T} \right)^{0.5}$			



**FIG. 1** shows the acting loads on the nozzles. The shear stress caused by the transverse force and the torsional moment at the nozzle-shell intersection are neglected, since it is assumed by this simple approximation that their contribution will normally not exceed 0.15  $f$ .

In case of doubt, the maximum total shear stress in the shell at the outer diameter of the nozzle should be calculated according to clauses 16.4.5.7 and 16.5.5.7, respectively, of EN 13445-3:2014 / A8:2019<sup>7</sup>, or alternatively according to PD 5500 clause G.2.8.2.3 (f) and G.2.8.3.3 (f)<sup>2</sup>. If it appears that the limit of 0.15  $f$  is exceeded, a more rigorous analysis should be considered. The applicable formulas for calculating the permissible individual nozzle loads are included in **TABLE 1**. Nomenclature is listed in **TABLE 2**.

**Note:** In the case of relatively thin-walled nozzle necks—i.e., the ratio of shell thickness and nozzle neck thickness exceeding 1—it is recommended to divide the permissible individual loads at the nozzle-shell intersection by that ratio (**TABLE 3**). This is due to the possibility that the stress in the nozzle neck may be a determining factor.

**Assessment protocol.** The following step-by-step approach explains the roles of the vessel design engineer and the piping stress analyst.

Vessel design engineer:

- **Step 1:** The vessel design conforms to the applicable code or standard considering only internal design pressure.
- **Step 2:** The allowable individual loads for each process nozzle are calculated, including the flange.
- **Step 3:** The vendor/vessel manufacturer furnishes the individual allowable forces and moments for each process nozzle-vessel intersection, as well as for the nozzle flange, in a tabular form on the appropriate drawing of the relevant equipment item. Normally this should be done twice: in the preliminary bid phase, and in the final mechanical design phase.
- **Step 4:** The information compiled in Step 3 must be transferred to the piping stress analyst.

Piping stress analyst: The starting point for the piping stress analyst is the compliance of the connected piping with the applicable design code:

- **Step 5:** Determine exerted nozzle loads (piping reactions) using an accepted software program.
- **Step 6:** Prepare a summary of piping reactions for the relevant process nozzles.
- **Step 7:** Provide load interaction checks at each process nozzle-vessel intersection and flange connection. In practice, this often means a joint effort of the vessel design engineer and the piping stress analyst. Both

disciplines must be convinced that simultaneous action of internal pressure and external loads are acceptable.

Linear load interaction rules that apply are shown in **TABLE 4**. The result of the load interaction rules must be recorded in the piping stress report.

**Note:** In cases where the piping reactions are not permissible, re-routing of the piping system or rearrangement of the pipe supports should be considered. Often, discounting the

**TABLE 2. Nomenclature**

Symbol	Description	Unit
$F$	Axial force	N
$M_l$	Longitudinal moment	Nmm
$M_c$	Circumferential moment	Nmm
$M$	Meridional (bending) moment	Nmm
$\sigma$	Available stress intensity for external loads	MPa
$D_o$	Outside diameter shell/sphere	mm
$T$	Wall thickness shell/sphere	mm
$T_{pad}$	Thickness of reinforcing plate	mm
$D_n$	Outside diameter nozzle neck	mm
$D_{pad}$	Outside diameter reinforcing plate	mm
$P_d$	Internal design pressure	MPa
$P_r$	Rated pressure (ASME B16.5 or ASME B16.47)	MPa
$A$	Outside diameter of flange	mm
$B$	Inside diameter of flange	mm
$C$	Bolt circle diameter	mm
$t$	Flange thickness	mm
$G$	Effective sealing diameter	mm
$W$	Flange width: 0.5 (A-B)	mm
$K_f$	"Koves" factor	-
$d_{bh}$	Bolt hole diameter	mm
$d_{bh}^*$	Max [ dbh (1 - B/1000) ; 0.5 dbh ]	mm

**TABLE 3. Stress intensity left over for external nozzle loads**

**Stress intensity left over for external nozzle loads:** **Explanation:** Satisfies the elastic shakedown criteria of 3 f

$$\sigma = \left( 3 - 2 \frac{P_d}{MAWP} \right) f$$

$f$  = Design stress (MPa) according to the applicable design code

MAWP = Maximum allowable working pressure at the nozzle intersection (MPa)

**TABLE 4. Load interaction rules**

	Nozzle on spherical part of head	Nozzle on cylindrical shell
At nozzle-shell intersection	$\frac{F_{actual}}{F_{allowable}} + \frac{M_{actual}}{M_{allowable}} \leq 1$	$\frac{F_{actual}}{F_{allowable}} + \frac{M_l actual}{M_l allowable} + \frac{M_c actual}{M_c allowable} \leq 1$
At flange-facing nozzle	$\frac{F_{actual}}{F_{allowable}} + \frac{M_{actual}}{M_{allowable}} \leq 1$	

nozzle flexibility in the pipe stress analysis results in a drastic reduction of the piping reactions—this is certainly the case with relatively thin-walled pressure vessels where the nozzles are not equipped with reinforcing pads.

The pressure vessel nozzle is considered acceptable if the load interaction conditions are met. It is the author's view that the nozzle design according to the recognized codes/standards will provide a reasonable amount of piping-im-

**TABLE 5.** Design calculation

Nozzle mark	Nozzle N1 (on spherical part of head)	Nozzle N2 (on cylindrical shell)
	According to Eq. (16.4-6) of EN 13445-3	According to Eq. (16.5-2) of EN 13445-3
MAWP (MPa)	1.02	1.05

**TABLE 6.** Calculation schedule

Auxiliary values	Maximum allowable individual load of Nozzle N1 in spherical part of head without reinforcing plate	Maximum allowable individual load of Nozzle N2 in cylindrical shell without reinforcing plate
$C_{11} = \frac{(D_o - T)}{2T}$	160.5	99.5
$C_{21} = \frac{(C_{11})^{0.5}}{\pi \times T \times D_n}$	0.000793823	0.000980433
$C_{31} = \frac{4(C_{11})^{0.5}}{\pi \times T \times (D_n)^2}$	0.000006251	0.00001211
$C_{41} = \left(\frac{D_n}{2T}\right)^{0.5}$	5.03984	4.02399
$\sigma = \left(3 - 2 \frac{P_d}{MAWP}\right) f$	130.94 MPa	138 MPa

**Applicable formulas for individual loads at nozzle intersections**

$F = \frac{\sigma}{1.75 C_{21}}$	94,256 N	
$M = \frac{\sigma}{1.75 C_{31}}$	11,969,742 Nmm - 11,970 Nm	
$F = \frac{\sigma}{6 C_{21}}$		23,459 N
$M_l = \frac{\sigma}{1.5 C_{31}}$		7,597,027 Nmm - 7,597 Nm
$M_c = \frac{\sigma}{1.15 C_{31} \times C_{41}}$		2,462,523 Nmm - 2,463 Nm

Auxiliary value	Maximum allowable individual flange loads: Nozzle N1	Maximum allowable individual flange loads: Nozzle N2
$K_f = 1 + \frac{t^2 + (W - d_{bh}^*)^2}{2.6 t^2}$	3.3987	4.0831

**Applicable formulas for individual loads on nozzle flange**

$F = (P_r - P_d) \frac{\pi}{4} G^2$	92,661 N	38,144 N
$M = (P_r - P_d) \frac{\pi}{16} G^2 \times C \times K_f$	49,995 Nm	16,813 Nm

posed loading ability. The worked example here will demonstrate this approach.

**Worked example.** A pressure vessel with an outer diameter of 2,000 mm is equipped with torispherical heads (type korb-bogen, according to DIN 28013<sup>11</sup>). The wall thicknesses are net 10 mm. A flush nozzle with a nominal diameter of 12 in. (NB 300) is fitted to the cylindrical shell. The nozzle neck of this nozzle has a nominal thickness of 17.48 mm (corresponds to schedule 80) and is provided with a Class 150 welding neck flange (according to ASME B16.5). The bottom is equipped with a flush 20-in. nozzle (NB 500), of which the nominal neck thickness is 15.09 mm (Schedule 40) and is located in the middle of the curved part of the head. This nozzle is also equipped with a Class 150 welding neck flange.

The shell and head are made of ASTM A515 Grade 60 material, while the nozzle necks are made of ASTM A106 Grade B seamless pipe material. Both nozzle flanges are made of ASTM A105 forged material. The nozzle flange connections are provided with a spiral wound gasket according to ASME B16.20<sup>12</sup>. The pressure vessel has a design pressure of 10 bar and a design temperature of 200°C. The rated pressure of the Class 150 flange is 13.8 bar at 200°C. No corrosion allowance applies. The design code for this pressure vessel is EN 13445. The design stress is 126 MPa (two thirds the yield strength at 200°C).

- **Step 1:** The design calculation is performed by the vessel design engineer according EN 13445-3 considering only internal pressure (TABLE 5).
  - **Step 2:** The maximum allowable individual loads of Nozzle N1 located on the spherical part of the head and Nozzle N2 located on the cylindrical shell are determined. The calculation schedule is shown in TABLE 6.
  - **Step 3:** A summary of individual allowable flanged nozzle loads is shown in TABLE 7.
  - **Step 4:** Successively, the vessel design engineer must provide the piping stress analyst with the calculated allowable individual allowable loads. This implies that the vessel design engineer must make the summary of Step 3 available to the piping stress analyst.
  - **Step 5:** The pipe stress engineer performs the pipe stress analysis using software approved by the inspecting body and client. Determining the piping reactions is part of the pipe stress analysis.
  - **Step 6:** The pipe stress engineer successively makes a summary of the loads acting on the process nozzle (piping reactions). For the relevant nozzles N1 and N2, the loads in TABLE 8 have been derived from the formal pipe stress analysis.
  - **Step 7:** Perform load interaction checks for nozzles N1 and N2.
    - **Nozzle N1:** At nozzle-head intersection: utilization factor =  $0.9392 < 1 \rightarrow \text{OK!}$   
At flange facing: utilization factor =  $0.3218 < 1 \rightarrow \text{OK!}$
    - **Nozzle N2:** At nozzle- shell intersection: utilization factor =  $0.9739 < 1 \rightarrow \text{OK!}$   
At flange facing: utilization factor =  $0.2623 < 1 \rightarrow \text{OK!}$
- Conclusion: All piping reactions remain within acceptable limits.

**TABLE 7.** Summary individual allowable flanged nozzle loads

Nozzle-head intersection			Flange facing		
Nozzle	F (N)	M (Nm)	F (N)	M (Nm)	
N1	94,256	11,970	92,661	49,995	
Nozzle-cylindrical shell intersection			Flange facing		
Nozzle	F (N)	M <sub>i</sub> (Nm)	M <sub>c</sub> (Nm)	F (N)	M (Nm)
N2	23,459	7,597	2,463	38,144	16,813

**TABLE 8.** Summary of piping reactions

Nozzle mark	F (N)	M (Nm)	M <sub>i</sub> (Nm)	M <sub>c</sub> (Nm)
N1	11,750	9,750	-	-
N2	1,950	-	3,375	1,100

**Takeaway.** The protocol developed is ideal for processing in a spreadsheet. The worked example proves its applicability and is a guideline for the user. In addition, it lends itself well to implementation in an engineering specification. The advantage lies in the simplicity of the protocol and it provides a safe approach to the assessment of nozzle loads. Time is also saved when using the protocol and additional costs for strengthening the nozzles can be avoided. The protocol has an excellent track record over many years in the hydrocarbon processing industry (HPI). **HP**

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## Sensitivity analysis of a plug flow reactor

A sensitivity analysis study evaluates uncertainties in a model's output based on the changes in the input parameters of the model. A good sensitivity analysis model<sup>1</sup> should have the following properties:

- Adaptability to scale and shape. It is important to consider both the range of variation of the input and the form of its probability density function when determining the influence on the output.
- It should include the effect of variation of all parameters on the output, which would provide a more multi-dimensional approach to the analysis.
- The ability to be model independent. Models can be additive or linear, and the method should work regardless.
- Allowing grouped parameters to be treated as individual entities. The ability to interpret the results with agility is an essential feature.

Variations of the independent variables are made, and the impact on the outcome is examined. An output that changes significantly as the input changes from minimum to maximum is classified as sensitive. An insensitive or robust output is one where the output does not alter significantly. The credibility of a model is increased if its output remains consistent regardless of the variation in input parameters. By conducting a sensitivity analysis, ideal parameter settings can be determined for a model and the risks associated with them can be quantified. The repeated use of sensitivity analysis allows for a deeper understanding of the model's strengths and weaknesses. Having this

knowledge is key to recommending concepts or operational approaches.<sup>2</sup>

This article presents a sensitive analysis of a typical plug flow reactor. For a continuous flow, the plug flow reactor model represents a cylindrical geometry in which chemical reactions take place across the length of the reactor. These reactions inside the reactor can be projected with the model so that vital reactor parameters can be assessed.<sup>3</sup> In this article, an open source simulation tool DWSIM<sup>4</sup> is used to investigate the impact of varying the inlet parameters of the plug flow reactor (i.e., flowrate, temperature, pressure and volume) on the outlet parameter of hydrogen (H<sub>2</sub>) conversion to ammonia (NH<sub>3</sub>). User-defined ranges are used for varying these parameters incrementally. Changes in the independent variables lead to a change in the dependent variables. The collected data can be visualized in a variety of plots, which can then be examined.

**Theory.** A glossary of terms is seen in **TABLE 1**. The mass balance reaction for Component A in the plug flow reactor at steady state<sup>5</sup> is given by Eq. 1:

$$dF_A / dV = r_A \quad (1)$$

The molar flowrate of the component at any point in the reactor is defined<sup>5</sup> in terms of the conversion factor as Eq. 2:

$$F_A = F_{A0} (1 - X_A) \quad (2)$$

For turbulent flows in an open plug flow reactor, the pressure drop<sup>5</sup> is given by Eq. 3:

$$dP/dz = -v[f_F(32m/\pi^2 d_{tube}^5)] \quad (3)$$

For an adiabatic plug flow reactor,

the temperature at any point in the reactor<sup>5</sup> is given in terms of the conversion factor as Eq. 4:

$$T = T_0 + [C_{A0}(-\Delta H_{rxn})/\rho C_{pm}]X_A \quad (4)$$

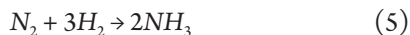
**Example.** The formation of NH<sub>3</sub> is examined for a first-order reaction using nitrogen (N<sub>2</sub>) and H<sub>2</sub> as the reactants. An equimolar mixture of H<sub>2</sub> and N<sub>2</sub> enters an adiabatic plug flow reactor at the rate of 3,000 kg/hr at a temperature of 400°C (752°F) and 200 bar. Simulation considers the volume of the plug flow reactor to be 1 m<sup>3</sup> with a length of 1 m.

**TABLE 1. Glossary of terms**

Parameter	Description
$F_A$	Molar flowrate of Component A
$V$	Volume of the reactor
$r_A$	Rate of reaction
$F_{A0}$	Initial molar flowrate for Component A
$X_A$	Conversion of the limiting reactant A
$P$	Pressure inside the reactor
$z$	Length of the reactor
$v$	Volumetric flowrate
$f_F$	Fanning friction factor
$m$	Constant mass flowrate
$d_{tube}$	Diameter of the plug flow reactor
$T$	Temperature inside the reactor
$T_0$	Temperature of the reactor at the entry point
$C_{A0}$	Initial concentration of the Component A
$C_{pm}$	Mass average heat capacity
$\rho$	Density
$\Delta H_{rxn}$	Heat of the reaction



For simplicity, the reaction is assumed to be a first-order, irreversible reaction (Eqs. 5 and 6):



$$r_{\text{N}_2} = K C_{\text{N}_2} \quad (6)$$

where  $K = 0.005$

$\text{N}_2$  is the base component for the reaction. Since the reactor is an adiabatic reactor, no heat goes into or exits the reactor; therefore, the value of energy term is zero.

**Simulation results and discussions.** Plug flow reactor simulations were con-

ducted with DWSIM software and values were calculated using steady-state assumptions. These results were obtained by using the Peng-Robinson thermodynamic package and entering the values given in the problem statement.

**TABLE 2** shows the results from the simulation of the plug flow reactor in DWSIM.<sup>6</sup>

**FIG. 1** depicts the pressure, temperature and concentration profile of the reactor. Over the length of the reactor,  $\text{N}_2$  and  $\text{H}_2$  concentrations will decrease as they combine to form  $\text{NH}_3$ , whose concentration will increase. Due to the

adiabatic nature of the plug flow reactor, which has no energy exchange with the surroundings, the temperature of the constituents inside the reactor rapidly increases over its length, reaching  $820^\circ\text{C}$  ( $1,508^\circ\text{F}$ ) before it exits the reactor. As the plug flow reactor only contains gases that are reacting over a small distance, there is only a small pressure drop along the reactor's length and the products leave the reactor at approximately the same pressure that they entered.

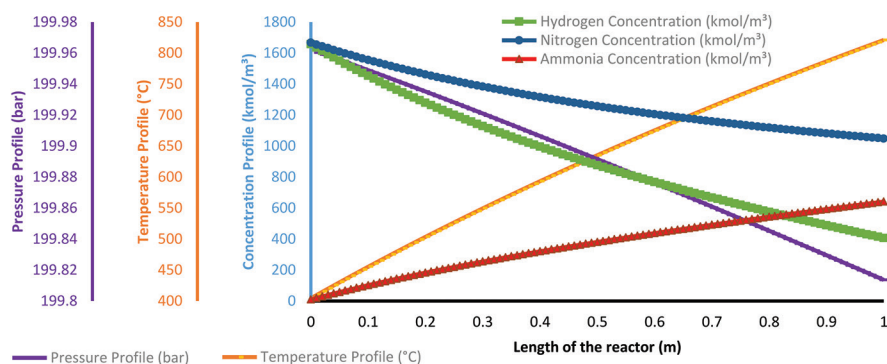
**Sensitivity analysis approach.** The sensitivity analysis was performed to investigate the effects of changing various parameters inside the plug flow reactor on the conversion of  $\text{H}_2$ . This simulation incorporated changes in feed temperature, feed pressure, feed mass flowrate and reactor volume over specified intervals. **FIG. 2** shows the variation in  $\text{H}_2$  conversion by changing the input parameters individually.

**Case 1: Variation of conversion of  $\text{H}_2$  with the inlet temperature of the feed.** In **FIG. 2**, the  $\text{H}_2$  conversion is shown as a function of the feed temperature, which varies between  $100^\circ\text{C}$  ( $212^\circ\text{F}$ ) and  $600^\circ\text{C}$  ( $1,112^\circ\text{F}$ ) without affecting any other parameters. It can be seen from the graph that  $\text{H}_2$  does not react until approximately  $240^\circ\text{C}$  ( $464^\circ\text{F}$ ). This is due to the fact that the activation energy required by the constituents to trigger the reaction has not yet been reached. The reaction takes place as soon as the threshold is crossed. Because the gases expand in the same amount of space in the plug flow reactor when the temperature of the inlet feed is increased, the conversion percentage slowly begins to decrease.

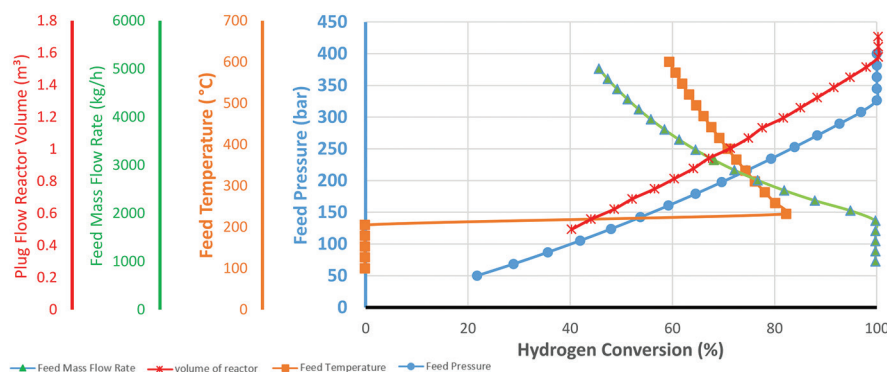
**Case 2: Variation of the conversion of  $\text{H}_2$  with the change in the pressure of the feed.** **FIG. 2** shows  $\text{H}_2$  conversion as a function of feed pressure, all other parameters remaining constant. The feed pressure varies between 50 bar and 400 bar. From the curve, it is evident that the  $\text{H}_2$  conversion percentage inside the reactor becomes increasingly higher as the feed pressure increases due to the gases being compressed as the feed pressure increases. In this reaction mixture, however, there is a point around 325 bar at which maximum conversion is achieved. In subsequent steps, the conversion of  $\text{H}_2$  is only slightly altered by increasing the pressure.

**TABLE 2.** Simulated results for the plug flow reactor

Parameter	Product	Feed	Units
Temperature	821.051	400	$^\circ\text{C}$
Pressure	199.852	200	bar
Mass flow	3000	3000	kg/hr
Molar fraction (mixture)/ $\text{H}_2$	0.193745	0.5	
Mass flow (vapor)/ $\text{H}_2$	59.7411	201.391	kg/hr
Molar fraction (mixture)/N	0.5	0.5	
Mass flow (vapor)/N	2142.47	2798.61	kg/hr
Molar fraction (vapor)/ $\text{NH}_3$	0.306255	0	
Mass flow (vapor)/ $\text{NH}_3$	797.792	0	kg/hr



**FIG. 1.** Pressure, temperature and concentration profile across the length of the reactor.



**FIG. 2.** Variation in the  $\text{H}_2$  conversion by changing input parameters individually.

**Case 3: Variation of conversion of  $H_2$  with the mass flowrate of the feed.** As a function of the mass flowrate of the feed, FIG. 2 illustrates the  $H_2$  conversion inside the plug flow reactor, other factors remaining constant. The mass flowrate of the feed varies from 1,000 kg/hr–5,000 kg/hr. As can be seen from the graph, at lower flowrates the plug flow reactor with a constant diameter sees less gas volume and, therefore, has the maximum conversion. Increasing the flowrate of the feed gradually causes the conversion percentage of  $H_2$  to decrease.

**Case 4: Variation of conversion of  $H_2$  with the volume of the plug flow reactor.** As a function of the volume of the plug flow reactor, FIG. 2 shows the change in the  $H_2$  conversion percentage with the other parameters remaining constant. The volume of the reactor varies between 0.5 m<sup>3</sup> and 1.7 m<sup>3</sup>. From the curve, it is evident that as the volume of the plug flow reactor increases, so does the  $H_2$  conversion. However, the  $H_2$  conversion percentage reaches a point when it can no longer be affected by subsequent reactor

volume increases once the maximum  $H_2$  conversion percentage is reached.

**Takeaway.** Various “what if” scenarios have been presented here based on a sensitivity analysis of a plug flow reactor. As a result of a systematic and detailed theoretical analysis, various parameters can be identified that allow for evaluation and the identification of optimum functional points, thereby decreasing costs as well as detecting complications during operations and enabling necessary precautions to avoid them. **HP**

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## Hydroprocessing catalyst selection—Part 1: Planning and selecting the catalyst evaluation method

Hydroprocessing catalysts are an essential part of any refinery involved in the treatment/conversion of most petroleum fractions ranging from naphtha to residue (FIG. 1). Hydrotreating catalysts help refiners meet fuel regulations and enhance the performance of downstream catalysts and processes [e.g., naphtha reforming or fluid catalytic cracking (FCC)] by removing sulfur, nitrogen and metals from their feedstocks as well as improving product properties by hydrogen addition. Moreover, hydrocracking catalysts further improve refiners' profits by converting low-value streams [e.g., vacuum gasoil (VGO)] into high-value fuels and chemical feedstocks. Therefore, selecting hydroprocessing catalysts requires great care to ensure maximum asset utilization and profitability.<sup>1</sup>

Part 1 of this article discusses pitfalls in planning and selecting the catalyst evaluation method and provides best practices to guide refiners towards an optimal hydroprocessing catalyst selection.

**Planning and invitation to bid (ITB) development.** Ideally, refineries should begin the catalyst selection process 18 mos–24 mos before the next catalyst change-out to provide sufficient time for all tasks involved. Typically, catalyst lead time is 6 mos–12 mos, leaving the rest for planning, evaluation and internal processing.<sup>2</sup>

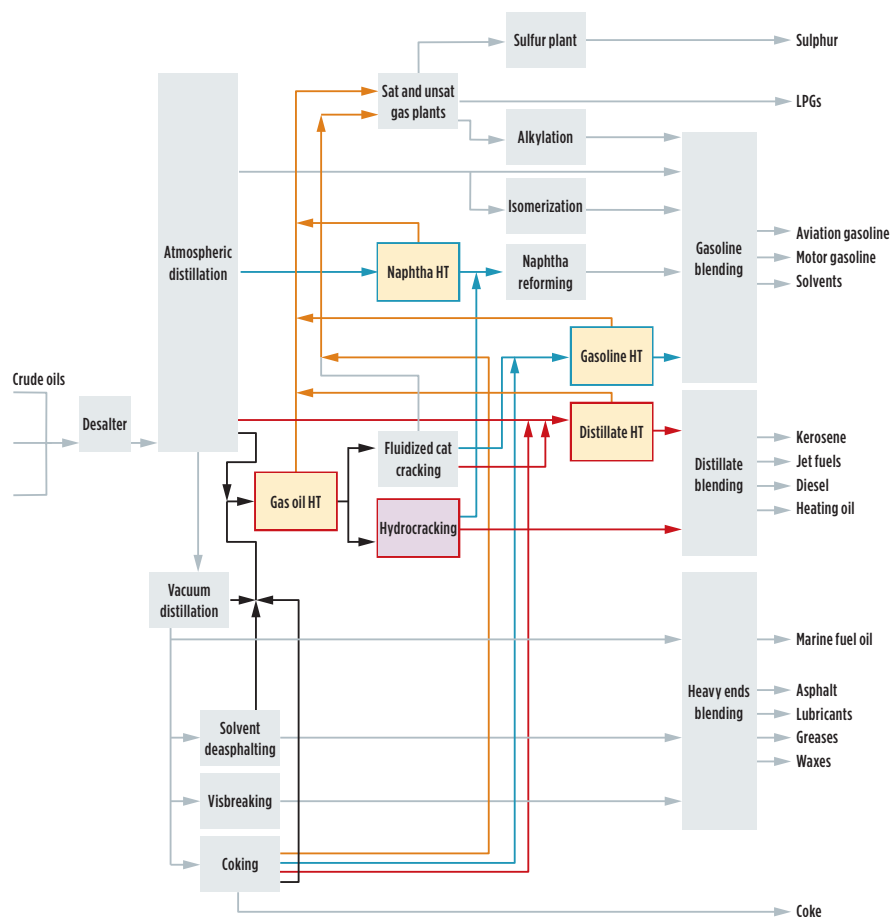
As a general practice, refiners should apply a multi-disciplinary approach to agree on catalyst requirements (e.g., longer run length or more difficult feedstocks). Additionally, the focal point (usually a unit process engineer) should incorporate current operating issues such as high reactor pressure drop or maldistribution into the ITB so the catalyst supplier can

properly address the problems in the next cycle. Most importantly, the economic direction should be clear (e.g., naphtha or middle distillates as preferred products).

Be realistic with feed qualities stated in the ITB. While being conservative will minimize the risks of not meeting the intended cycle length, being too conser-

vative can also underutilize the existing unit or even worsen unit performance in some instances.

For example, if metal contents stated in the ITB are too conservative, use the worst-case scenario for every metal species. This usually means the catalyst supplier will propose a larger portion of

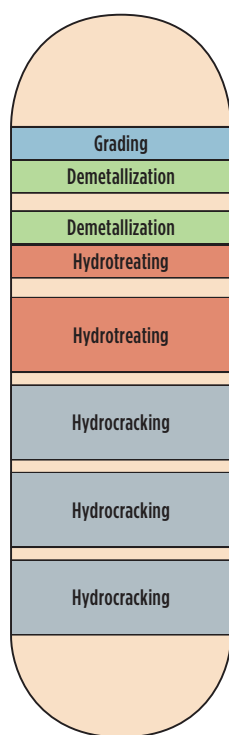


**FIG. 1.** In modern refineries, hydroprocessing improves the qualities and value of most petroleum fractions (highlighted in yellow and pink blocks).

**TABLE 1. Qualitative comparisons between two experimental approaches, conventional pilot-scale vs. high-throughput system**

Aspect	Conventional pilot-scale system	High-throughput system
Feed and catalyst shipment costs	Higher costs from more feed and catalyst requirements, 150 l (liters) of feed per one loading scheme (one test scenario)	Much lower, 20 l of feed per one loading scheme (one test scenario)
Number of catalyst loading schemes and time requirement	Limited catalyst loading schemes, usually require more time from limited reactors in parallel	Up to 16 parallel reactors: an attractive option when catalyst loading schemes exceed four; usually require less time as there are more available reactors in parallel
Catalyst homogeneity	Statistically less affected by non-homogeneity due to a larger reactor volume	Practically no issue with good catalyst screening
Feed storage and control	Has a dedicated feeding section for each reactor, possible to process different feedstocks in parallel	Common feeding section, therefore the same feedstock for all reactors in parallel (distributed via the flow distribution device); distribution quality affects mass balance errors
Product analysis	Takes less time for the same sample amount: an ideal choice when frequently varying process conditions or analyzing detailed product properties	Takes more time for the same sample amount; requires close monitoring and control to ensure sample's uniformity
Nitrogen slip control*	Directly measured from interstage sampling	Indirectly measured via a mirror parallel pretreating reactor <sup>1</sup>
Recycle operation*	Possible but may not be accessible by the majority of refiners; primarily available in licensing/catalyst companies	Impractical, mainly from difficulties in flow control, e.g., smaller recycle flowrate
Testing fee	Not necessarily more expensive	Not necessarily cheaper

\*Specifically for hydrocracking applications



**FIG. 2.** A simple loading scheme of a six-bed hydrocracking reactor (not to scale), where grading materials and demetalization catalysts—highlighted in light blue and green, respectively—protect the hydrocracking reactor against high pressure drop and rapid metal deactivation.

demetalization catalysts (lower activity), which will, in turn, limit the volume of the main hydrotreating catalysts (higher

activity) for a fixed reactor volume (see an example of a typical loading scheme in FIG. 2). As such, the refiner might miss out on opportunities to process more difficult feeds or increase the unit throughput from unrealistic metal uptake requirements. Incorporating past spent catalyst analyses (for both metal and particle size distribution) along with actual feed qualities will help refiners develop realistic grading and demetalization volume requirements. Nevertheless, refiners should be careful when balancing risks and opportunities.

Clearly communicate with catalyst vendors about unit configurations and constraints. The authors have seen a diesel hydrotreating catalyst vendor that once designed the catalyst loading scheme without realizing there was no amine scrubber in the recycle gas loop until the catalysts were later put under operation.

**Catalyst evaluation methods.** While some refiners still rely on vendor estimations/predictions, independent catalyst testing has become more popular as a tool to reveal the actual catalyst performance. This evaluation approach is particularly crucial to a critical unit like a hydrocracker, where a slight difference in product yield can result in multi-million dollars of profit/loss per year.

In contrast with a general notion, comparing paper estimates/predictions from different catalyst vendors is not an

apples-to-apples comparison; nonetheless, this is prevalent among refiners due to its simplicity. In fact, catalyst vendors employ different design assumptions, feed characterization techniques, kinetic models and product property estimators, such as basic to non-basic nitrogen ratio or aromatics distribution. Consequently, it is fundamentally incorrect to compare estimates/predictions between catalyst vendors. Sadly, many refiners are unaware of this fact.

To make matters worse, some catalyst vendors are more aggressive than others. It is not uncommon to see catalyst vendors distort results from their kinetic model to make their proposal more attractive. The authors worked with a diesel hydrotreating catalyst supplier that proposed a close-to-nil offgas yield without any logical explanation. When this was challenged as impossible, the supplier nonetheless confirmed that it was a result of their kinetics model. This is a perfect example of how refiners should always be skeptical of data presented in vendors' proposals and how paper-based evaluation can be subjective.

Despite these shortfalls, it is still acceptable to use paper-based evaluation for less critical applications, such as a naphtha hydrotreater, although the best practice is to have your catalysts tested before the actual reloading.

For refiners without an in-house catalyst testing facility, several companies can



provide an independent catalyst testing service. Two available primary approaches are presently in use: a conventional pilot-scale system and a high-throughput system (FIGS. 3A and 3B, respectively).

Each method has its advantages/disadvantages, as summarized in TABLE 1. Refiners must select the best independent catalyst testing laboratory to suit their requirements and constraints. While the authors' experience confirmed that both approaches provided essential information for hydrocracking catalyst benchmarking,<sup>1,3</sup> many refiners favor some laboratories more than others. It is recommended to proactively contact these independent laboratories as soon as the new cycle starts. One laboratory requires at least 24 mos of pre-booking before the actual test date. Generally, a typical catalyst testing campaign could last between 1 mos and 3 mos, but this may vary upon the number of test scenarios.

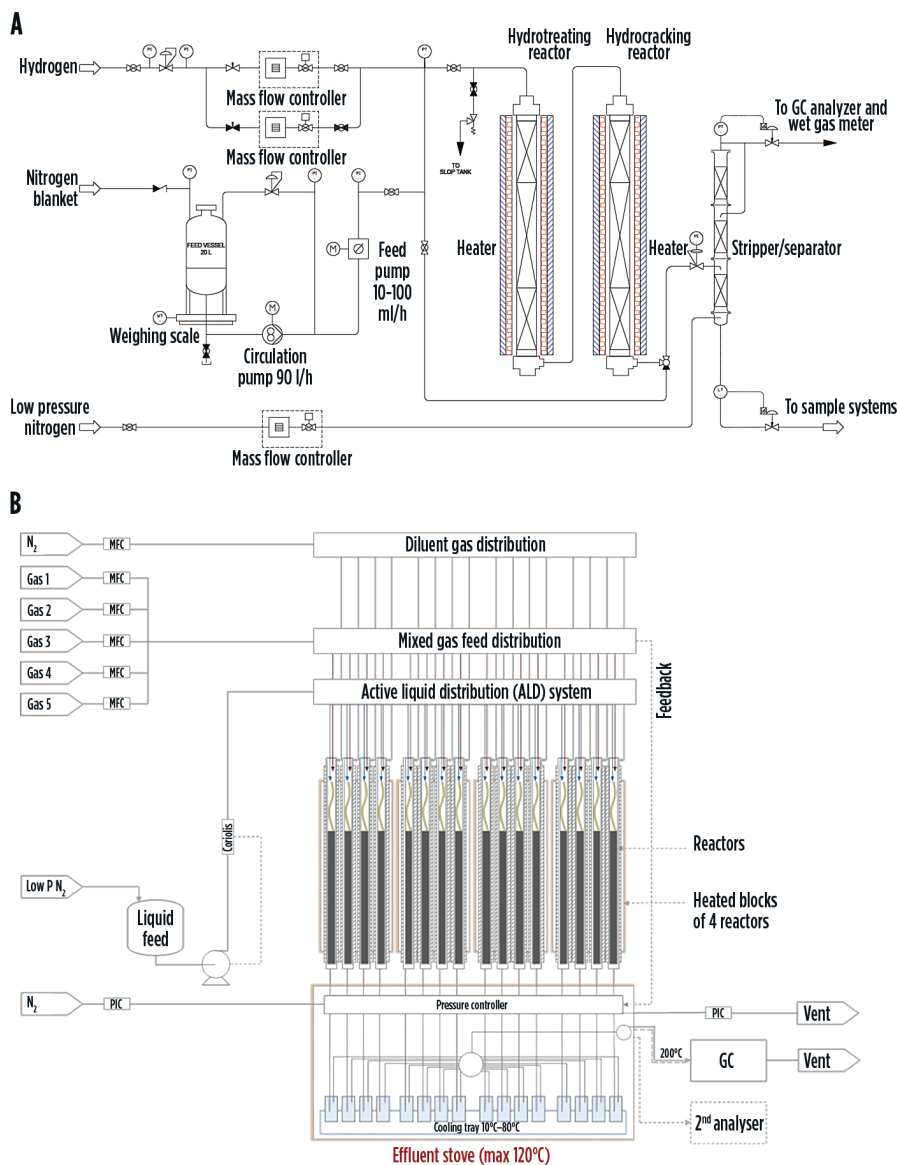
From the authors' recent experience, the testing fee for each catalyst loading scheme (hydrocracking, one-test scenario) can range between \$40,000 and \$95,000. In general, the service fee for a hydrotreating catalyst testing campaign is less expensive than a hydrocracking one, as it is less complicated. A more important question is who will pay for the test. The refiner may pay for the total cost or ask the catalyst suppliers to share. In general, the willingness of the catalyst supplier to share the cost increases with the value of the catalyst package.

**Takeaway.** On the surface, independent catalyst testing seems costly. However, the service fee is often trivial compared to the opportunity to distinguish the best catalyst supplier from an average one. In the authors' recent experience, a performance gap for a 54,000-bpd hydrocracker could be up to \$20 MM/yr.

In the June issue of *Hydrocarbon Processing*, Part 2 will discuss critical aspects of a hydroprocessing catalyst testing program and present best practices/suggestions to ensure a successful catalyst benchmarking campaign. **HP**

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**FIGS. 3A AND 3B.** A conventional pilot-scale (A) vs. high-throughput bench scale system (B). Courtesy of Avantium.

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Complete literature cited available online at [www.HydrocarbonProcessing.com](http://www.HydrocarbonProcessing.com)

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## The 1960s: Synthetic oils, zeolite catalysts, LLDPE, OPEC and creation of the PLC

During the 1960s, the global refining and petrochemical industries witnessed new processes and products that enhanced the daily lives of millions of people around the world. The decade was responsible for the creation of new petrochemical products to provide better and more durable goods within many industrial sectors and consumer goods applications. Other innovations, such as the creation of synthetic oils and synthetic zeolite catalyst, enhanced processing operations and engine/fuel performance in the automobile and aviation sectors. The 1960s was also a prominent decade for LNG trade [the first transatlantic LNG cargo was carried on the *Methane Pioneer* in early 1959 from Constock's LNG production facility in Louisiana (U.S.) to the UK; the UK also received the world's first commercial LNG cargo from Shell's *Methane Pioneer* vessel in October 1964 from Algeria; LNG exports from Alaska (U.S.) to Japan commenced in the late 1960s],<sup>96</sup> the creation of the programmable logic controller (PLC)—a significant evolution in automation—and the creation of the Organization of Petroleum Exporting Countries (OPEC), which was, and still is, a major force in setting global oil prices.

**Creation and widespread adoption of synthetic oils.** Although the first synthetic hydrocarbon oils were produced in 1877 by French chemist Charles Friedel and American chemist James Mason Crafts (i.e., Friedel-Crafts alkylation and acylation reactions), synthetic oils did not see widespread adoption until post-World War 2 (WW2).

Prior to WW2, several individuals developed new reactions to produce synthetic oils. These included German scientists Friedrich Bergius, Franz Fischer and Hans Tropsch (the Bergius and Fischer-Tropsch

processes were detailed in the History of the HPI segments published in the January and March issues of *Hydrocarbon Processing*), as well as American researcher F. W. Sullivan while working at Standard Oil of Indiana (U.S.). Sullivan's team tried to commercialize synthetic oils in 1929; however, this attempt was challenged due to lack of demand. Regardless, Sullivan published a paper in 1931 titled "Synthetic lubricating oils relation between chemical constitution and physical properties," which, along with research from the German chemist Hermann Zorn, provided a foundation for the future widespread use of synthetic oils in the aviation and the automobile sectors—Zorn and his team researched more than 3,500 synthetic esters during the early 1940s to find an alternative to petroleum oil to help fuel Germany's war machine.<sup>97,98</sup>

The need for synthetic oils did not materialize until Germany's invasion of the Soviet Union during WW2. During the Battle of Stalingrad, the harsh Russian winter demobilized German tanks, fighter planes and other military vehicles. The main culprit: temperature. Conventional petroleum oil could not stand up to the frigid temperatures during the harsh Russian winter. These oils were produced through conventional distillation, which has several drawbacks, including solidifying in low temperatures, rendering its use extremely ineffective in extremely cold environments—conventional distillation could not completely remove impurities such as waxes, which would solidify in cold temperatures, leading to the inability of engines to start.<sup>98</sup> This event demonstrated that a new form of lubricating oil was needed.

The use of synthetic oils found its demand within aircraft engines during and post-WW2. While Zorn was conduct-

ing widescale tests on different synthetic esters in Germany, American chemist William Albert Zisman was researching synthetics at the Naval Research Laboratory in Washington D. C. (U.S.). His work (1942–1945)—detailed in the technical article "Synthetic lubricant fluids from branched-chain diesters physical and chemical properties of pure diesters,"<sup>99</sup>—led to the development of the first diester synthetic base oils, a precursor to the development of modern synthetic lubricants.<sup>98,100</sup> With the creation of the jet engine in the 1940s (the history of the jet engine was detailed in the History of the HPI segment published in the February issue of *Hydrocarbon Processing*), synthetic oils were able to protect engine components against extreme temperatures during flight, a challenge that conventional oils could not accomplish. As a result,



**FIG. 1.** Albert Amatuzio developed the world's first synthetic motor oil to meet API service requirements. For this, he is known as a pioneer in synthetic lubrication. Photo courtesy of AMSOIL.

synthetic oils were used for military and commercial air travel.

It was not until the 1960s that the idea of using synthetic oils in the automobile industry could provide significant benefits to engine performance. American pilot and inventor Albert Amatuzio conducted research in the 1960s on the use of synthetic lubricants in automobile engines. As a squadron commander in the Minnesota Air National Guard and WW2 fighter pilot (he flew America's first operational fighter jet, the F80 Shooting Star),<sup>101</sup> Amatuzio was aware of the benefits synthetic lubricants provided aircraft engines. His goal was to find a way for automobile engines to gain the same lubricating benefits.

In 1966, Amatuzio formulated his first synthetic motor oil, testing it in his colleague's new 1966 Ford station wagon.<sup>98</sup> After the successful test, he continued to develop new synthetic oils and sell them throughout the late 1960s under the name AMSOIL. However, the public was slow to adopt Amatuzio's new synthetic motor oil despite the many benefits it provided vs. conventional lubricating oils. The primary challenge was price, as synthetic motor oil costs several times more than conventional motor oil.<sup>98</sup>

Seeking additional validation of performance standards established by the American Petroleum Institute (API) and the Society of Automotive Engineers, Amatuzio had his motor oil tested by a third-party laboratory in 1972. After rigorous tests, AMSOIL Synthetic Motor Oil became the world's first synthetic motor oil to meet API service requirements.<sup>98</sup> This validation, along with major oil companies producing their own synthetic lubricating oils for the auto industry, would eventually lead to widespread adoption of synthetic motor oils for automobiles.



**FIG. 2.** The delegation of Saudi Arabia at the historic Baghdad Conference in mid-September 1960. Photo courtesy of OPEC.

After Amatuzio's accreditation and continued sales of his novel product, Mobil followed suit, creating the first Mobil 1 fully synthetic motor oil in 1971—the company first introduced Mobilgrease 28 (still in use) in the early 1960s to prevent military plane wheel bearings from failing during landings in cold temperatures, followed by the Mobil-brand synthetic oil technology for big diesel engines powering oil drilling rigs on Alaska's North Slope (U.S.) in temperatures as low as  $-40^{\circ}\text{C}$  in the late 1960s.<sup>102</sup>

**The formation of OPEC.** Following WW2, global oil consumption began to expand significantly. During this timeframe, the U.S. was simultaneously the world's largest consumer and producer of oil, and global oil supplies were dominated by the Seven Sisters (five were headquartered in the U.S.)—Anglo-Iranian Oil Co. (now bp), Royal Dutch Shell, Standard Oil Co. of California (now Chevron), Gulf Oil and Texaco (both merged into Chevron), Standard Oil Co. of New Jersey and Standard Oil Co. of New York (both are now ExxonMobil). Up until the early 1970s, these multinational organizations controlled approximately 85% of the world's petroleum reserves—this included large oil reserves in the Middle East.<sup>103</sup>

Wanting to control more of its domestic reserves, several oil exporting countries—Iran, Iraq, Kuwait, Saudi Arabia and Venezuela—convened in Baghdad, Iraq in September 1960 (**FIG. 2**). This historic meeting's (the Baghdad Conference) goal was to discuss ways to increase crude oil pricing produced by these countries, as well as ways to respond to unilateral actions by the Seven Sisters and other multinational organizations.<sup>103</sup> This meeting led to the creation of the Organization of Petroleum Exporting Countries (OPEC), which witnessed its member countries increase over the next 15 yr.

OPEC grew in prominence during the 1970s, as its member countries gained greater control of their domestic production and began to play a greater role in world oil markets.<sup>104</sup> The organization still plays a decisive role in crude oil production, with the ability to significantly affect crude oil pricing globally.

During the 1960s, the Middle East also witnessed the expansion of regional refining and petrochemical capacity. For example, the Ras Tanura refinery in Saudi

Arabia expanded its capacity from 50,000 bpd to 210,000 bpd.<sup>69</sup> Kuwait National Petroleum Co. expanded the Mina Abdullah refinery's capacity from 30,000 bpd to 145,000 bpd in 1963, as well as commissioned the 95,000-bpd Shuabia refinery in April 1968—the Shuabia refinery increased processing capacity to 195,000 bpd in 1975. The Shuabia refinery eventually closed in 2017; however, its infrastructure was incorporated into the country's capital-intensive Clean Fuels Project.<sup>105</sup> The Shuaiba Industrial Zone also housed Kuwait's first chemical fertilizer complex. Petrochemicals Industries Co.—established in 1963—commissioned the facility in 1967, which was the first of its kind in the Middle East. Saudi Arabia and Qatar followed suit, establishing the Saudi Arabian Fertilizer Co. in 1965 and the Qatar Fertilizer Co. in 1969.<sup>106</sup>

**Synthetic zeolite catalysts are patented and commercialized.** The term zeolite—microporous, aluminosilicate minerals—was first coined by Swedish mineralogist Axel Fredrik Cronstedt in 1756.<sup>107</sup> Cronstedt, who is most noted for discovering the elements nickel and scheelite (later to be known as tungsten), discovered zeolite after heating the mineral stillbite (tectosilicate minerals of the zeolite group) with a blowpipe flame. The process produced a large amount of steam from water that had been absorbed by the mineral.<sup>107,108</sup> After observing the reaction, Cronstedt coined the mineral “zeolite” from the Greek words “to boil” and “stone.”<sup>107</sup>

Modern research and development of synthetic zeolites were pioneered by individuals such as New Zealand-born chemist Richard Barrer (his work in adsorption and synthesis began the era of synthetic zeolites); Robert Milton, Donald Breck and T. B. Reed at Union Carbide (their work during the late 1940s/early 1950s led to the discovery of synthetic zeolites A, X and Y); and Jule Rabo and Edith Flanigen who both worked with Milton's team at Union Carbide. Rabo led the catalyst research group at Union Carbide from 1957–1961 and played a key role in the discovery of the catalytically active ingredient used worldwide in the catalytic cracking of gasoils to produce gasoline.<sup>109</sup> Flanigen was instrumental in the development of zeolite Y. In his historical perspective on zeolite research, Milton described



Flanigen as a world expert on zeolite synthesis and the first to synthesize high-silica Y with silica/alumina ratios above 4, the first to remove aluminum from zeolite lattices without loss of structure, and responsible for identifying and evaluating the myriad of samples from Union Carbide's investigation of sedimentary zeolite deposits in the Western U.S.<sup>109</sup> Dr. Flanigen's work was detailed in the Industry Pioneers segment published in the April issue of *Hydrocarbon Processing*.

In the 1950s, while working at Mobil Oil, American chemical engineers Charles Plank and Edward Rosinski were researching various catalysts. During their research, they decided to test zeolite as a catalyst for catalytic cracking. Plank and Rosinski's research on zeolite catalysts showed superior activity and selectivity, which led to dramatically higher gasoline yields during the cracking process. According to literature, the increased gasoil conversions could also be obtained without increasing gas or coke yields—two unwanted byproducts of cracking.<sup>110,111</sup>

The two chemists submitted their patent—*Catalytic cracking of hydrocarbons with a crystalline zeolite catalyst composite*—to the U.S. Patent Office in July 1960.<sup>111</sup> The patent submission and subsequent literature written by Plank described the catalyst as consisting of a finely divided crystalline aluminosilicate, having uniform pore openings between 6 ångströms (Å) and 15 Å, dispersed in an inorganic oxide matrix with a low sodium content.<sup>111,112</sup>

The technology patent was approved on July 7, 1964. Plank and Rosinski's patent laid the foundation for modern catalytic cracking. Due to its molecular structure, zeolite catalysts are extremely effective in the reaction process—they have higher performance at lower pressures.

Five years after Plank and Rosinski's patent was approved, Robert Argauer and George Landolt—the two also worked at Mobil Oil—were the first to synthesize high-silica zeolite, which was commercially named Zeolite Socony Mobil-5 (ZSM-5). The two submitted the technology for a U.S. patent in 1969. The patent submission *Crystalline zeolite ZSM-5 and method of preparing the same* provided a detailed analysis of the novel crystalline aluminosilicate zeolite and its usefulness in cracking and hydrocracking processes, as well as within other refining processes

(e.g., alkylation, isomerization) and petrochemical products production.<sup>113</sup> ZSM-5 catalysts are still used in refining and petrochemical plants around the world.

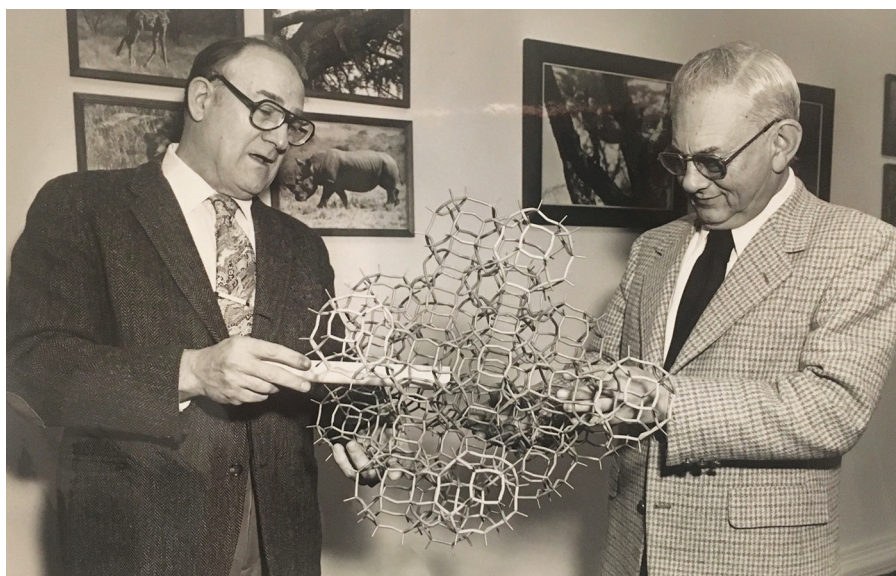
**New petrochemical products/processes enhance everyday life.** Several new petrochemical products were discovered in the 1960s. These included Kevlar, linear low-density polyethylene (LLDPE) resins, a more cost-effective process to produce acrylonitrile and stretched polytetrafluoroethylene (PTFE), which came to be known as Gore-Tex. With the significant expansion in the global petrochemical industry, *Petroleum Refiner* retitled the technical publication to *Hydrocarbon Processing and Petroleum Refiner* in 1961, then adopted the name *Hydrocarbon Processing* in June 1966. The publication's title—*Hydrocarbon Processing*—represented the integration of the global refining and petrochemical industries and the technical processes and operational know-how that are synonymous with refinery and petrochemicals production.

**Acrylonitrile.** The origins of acrylonitrile trace back to 1893 when French organic chemist and pharmacist Charles Moureu was the first to synthesize acrylonitrile. However, acrylonitrile did not find a commercial use until the 1930s—industrial producers used the material in applications such as acrylic fibers for textiles and synthetic rubber.<sup>114</sup>

Although the use of acrylonitrile was extremely effective in several applications, production was expensive and included multistep processes. In the late 1950s, the Standard Oil Co. (Sohio, later bp) discovered a cheaper processing route through selective catalytic oxidation to produce acrylonitrile. This research effort was led by Franklin Veatch. Veatch proposed that converting light refinery gases (e.g., aliphatic hydrocarbon propane) to oxygenates could be profitable. In 1953, funding was approved, and Veatch and his team began research efforts. With only 6 wk left of funding, Veatch's research team made a vital discovery when conducting a test run on propylene over a modified vanadium pentoxide oxidant, resulting in the production of acrolein—an additional oxidation step would produce acrylic acid.<sup>114</sup>

In 1955, the Sohio research team began testing oxidants as direct oxidation catalysts, leading to the process of converting propylene to acrolein in a single catalytic reaction step—the process used a bismuth phosphomolybdate catalyst.<sup>114</sup> According to literature, acrylonitrile was produced by feeding propylene, ammonia and air over the bismuth phosphomolybdate catalyst. The process resulted in ammoxidation (i.e., the Sohio process), which produced a 50% yield of acrylonitrile, with acetonitrile and hydrogen cyanide as coproducts.<sup>114,115</sup>

Approximately 4 yr after the start of research, the Sohio process was commer-



**FIG. 3.** Rosinski (left) and Plank (right) demonstrate their invention of zeolite catalyst prior to being inducted into the National Inventors Hall of Fame in 1979. Photo courtesy of the National Inventors Hall of Fame.



cialized and a new \$10-MM, 47.5-MMlb/yr plant was constructed in Lima, Ohio (U.S.). The plant was commissioned in early 1960. Upon the success of the Lima plant, Standard Oil Co. began licensing the Sohio process for the cost-effective production of acrylonitrile.

Acrylonitrile is used in numerous applications that touch the everyday lives of people around the world. It is a key ingredient in acrylic fibers (used in the production of clothing, carpeting, industrial yarns, blankets and drapes, among several other applications); in acrylonitrile-butadiene-styrene to produce appliances, automobile components, sports equipment, telephone and computer casings; specialty chemicals; polyols; nitrile rubber to produce fuel hoses, automotive belts and hoses; plastic resins; and adhesives and coatings.<sup>114</sup> The global acrylonitrile mar-



**FIG. 4.** Stephanie Kwolek and others of the DuPont group that developed Kevlar. From left to right: Kwolek, Herbert Blades, Paul Morgan and Joseph Rivers. Photo courtesy of DuPont.

ket reached approximately \$12 B in 2020, with forecasts showing growth to more than \$16 B by the late 2020s.<sup>116,117</sup>

**Kevlar.** After graduating college in the mid-1940s, American chemist Stephanie Kwolek took a job with DuPont. During the 1950s/1960s, Kwolek's focus was on research and development of new synthetic fibers capable of performing in extreme conditions. Her initial research focused on aromatic polyamides—a type of polymer that can be made into strong, stiff and flame-resistant fibers.<sup>118</sup> This work extended into the study of the polymers poly-p-phenylene terephthalate and polybenzamide. The focus of her team's research was to discover a new lightweight, strong fiber to use for light, strong tires (**FIG. 4**).<sup>119</sup>

During one experiment in 1965, Kwolek noticed the solution she was working on had a cloudy, thin and opalescent look when stirred, along with a low viscosity. According to literature, she also noticed that under certain conditions, many rodlike polyamides would line up in parallel (i.e., form a liquid crystalline solution), which could be spun into oriented fibers.<sup>120</sup> Upon testing the solution in a spinneret, Kwolek noticed that the fibers that were created were incredibly stiff and strong—these fibers had a high tensile strength-to-weight ratio (i.e., this new substance was five times stronger than steel on an equal weight basis).<sup>119</sup> Her discovery created a whole new field of

polymer chemistry, which eventually led to the creation of modern Kevlar in 1971.

Kevlar's first commercial use was as a replacement for steel in racing tires in the 1970s. Since then, Kevlar has been used in more than 200 applications, including sporting and safety equipment, cables/ropes, boats, airplanes, motor vehicles, satellites, household items, and, most notably, in bullet-proof vests. In fact, on the day Kwolek passed away (June 18, 2014), DuPont announced that the one millionth Kevlar bullet-proof vest had been sold.<sup>121</sup> For her contribution to polymer research, Kwolek was the first woman to earn the Lavoisier Medal for Technical Achievement from DuPont.

**LLDPE.** In 1954, DuPont Canada was split off from its parent company Canadian Industries Ltd. The new company's first objective was to establish a research laboratory in Kingston, Ontario, Canada to identify new growth businesses, one of them being new applications for polyethylene (PE) production. The Kingston Research Center team focused on producing low-density resins by incorporating large amounts of alpha-olefin comonomers.<sup>122</sup> However, the product produced from pilot plant testing—which later became known as LLDPE—behaved differently than conventional low-density resin processes at the time, along with several other production challenges. Despite these setbacks, DuPont Canada greenlighted an investment in a new PE production plant.

Due to the economic market conditions in the late 1950s, DuPont Canada could only invest capital in one PE production plant. This facility—located in Corunna, Ontario (outside Sarnia)—could produce both high- and low-density PE (HDPE/LDPE).<sup>122</sup> The 275-MMlb/yr St. Claire River (SCLAIR) site—commissioned in 1960—used the same process produced in pilot plant testing by the Kingston Research Center team; thus, establishing the first commercial plant to produce LLDPE. The resin—named SCLAIR after the production site's location—was found to be stiffer, more heat resistant and tougher than conventional LDPE.<sup>123</sup> Several modifications to optimize the process were completed over the next several years, providing resins that would fetch premiums beyond commodity market prices.<sup>122</sup> The plant was so successful that DuPont Canada added a second PE pro-



**FIG. 5.** The Bedford Associates group, who formed Modicon in 1968 after developing the world's first PLC, the Modicon 084. Left to right: Dick Morley, Tom Boissevain, George Schwenk and Jonas Landau. Photo courtesy of Schneider Electric.

duction line at the Corunna site in 1976, followed by licensing the SCLAIRTECH process worldwide in 1980—the technology can produce a range of products from LLDPE to HDPE.<sup>124</sup> DuPont Canada's PE business, including the St. Claire PE plant, was eventually purchased by Nova Chemicals in 1994.

In the 1970s/1980s, several other companies began to produce their own LLDPE resins. These included Dow Chemical, Union Carbide and bp Chemicals, among others. Union Carbide's LLDPE technology's origins emerged from research and development on a low-pressure, gas-phase fluidized bed process to produce HDPE. This process—known as the UNIPOL PE process (now licensed by Univation Technologies)—came to fruition in 1968 with the startup of the G-1000 plant in Seadrift, Texas (U.S.). The UNIPOL process extended its reach into LLDPE production in 1977.<sup>125</sup> By the late 1980s, more than 70% of the world's LLDPE production was produced via gas-phase polymerization—the basis of the UNIPOL process.<sup>123</sup> Today, several additional companies license their own LLDPE process, including Borealis, Chevron Phillips Chemical, INEOS and LyondellBasell, among others. LLDPE is used in many consumer goods such as plastic grocery/trash bags, shrink wrap, toys/playground and plastic gardening equipment, tubing, flooring and many other applications. Over the past 60 yr, the LLDPE market has significantly expanded, with forecasts showing the global LLDPE market will exceed \$65 B by the mid-2020s and increase to more than \$85 B by 2030.<sup>126,127</sup>

**Gore-Tex.** In the late 1950s, Bill Gore left his job at DuPont to pursue detailed research and analysis on the untapped potentials of PTFE.<sup>128</sup> The polymer PTFE was discovered by accident in the late 1930s by Roy Plunkett who was working at DuPont at the time. This discovery eventually led to the development of Teflon—the discovery of PTFE and the subsequent creation of Teflon was detailed in the History of the HPI segment published in the February issue of *Hydrocarbon Processing*.

In 1969, Bill's son Robert (Bob) conducted experiments by heating rods of PTFE and stretching the material. However, on one such occasion, primarily out of frustration, he yanked the heated

PTFE rod, causing it to stretch about 800%. After analysis, he noticed that the resultant material was incredibly strong, microporous (the structure was approximately 70% air), and contained several key benefits, such as low water adsorption and good weathering properties.<sup>128,129</sup> The expanded PTFE (ePTFE) was given the name Gore-Tex and sold commercially in the 1970s as a breathable, waterproof and windproof fabric for clothing (e.g., jackets).<sup>129</sup> Gore-Tex (ePTFE) found use in many applications over the ensuing decades, including in insulation, medical implants, high-performance fabrics, gloves, footwear and even on astronauts' spacesuits.

**The PLC revolutionizes industrial automation.** The invention of the PLC originated within the automotive industry. In the late 1960s, Bedford Associates—from Bedford, Massachusetts (U.S.)—was awarded a contract from GM Hydramatic [the automatic transmission division of General Motors (GM)]. GM wanted to replace its hardwired relay systems with a better electronic device.<sup>130</sup> Hardwired relay systems had several disadvantages: several relays were needed to control a single device, improper wiring of only one relay could cause the machine or entire system to shut down, systems were hard to troubleshoot and fix, and needed changes to the system often required reconfiguring the entire system.<sup>131</sup>

In 1968, the founder of Bedford Associates, Richard (Dick) Morley (known as the father of the PLC), unveiled the world's first PLC, the Modicon 084 (FIG. 5)—the technology was named Modicon (MODular DIGital CONTroller) 084 since it was the company's 84th project.<sup>132</sup> The creation of the PLC meant that large banks of relays could be replaced by a single device. It also contained enough memory to retain loaded programs in the event of a power outage and worked well in harsh conditions.<sup>131</sup>

Bedford Associates soon adopted the company name Modicon and began to market PLCs. The company was also responsible for the invention of the Modbus in the late 1970s—Modbus is a data communications protocol that enables electronic devices to communicate with each other.<sup>133</sup>

Modicon was acquired by Gould Electronics in 1977 and then by AEG in

1989. The company eventually became part of Schneider Electric in 1994 with the merger of AEG and Groupe Schneider—the merger took the name Schneider Electric in 1999.<sup>134</sup>

The invention of the PLC created a new era in automation technology. Today, PLCs are incorporated into refining and petrochemical plant operations to help monitor plant equipment, among other production actions. **HP**

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## Excerpts from the 1960s: Petrochemicals rise in prominence and new know-how in refining processes

### Old units do explode!

O. A. Pipkin, January 1960

This is the full story of the explosion that rocked the refinery of Cities Service in January 1959—the result of a series of human errors. Who would have thought that such a potential hazard existed in a coking process operating for more than 30 yr?

### How well do you supervise?

J. E. Bigham, February 1960

Good supervisors should know the limits of their authority and responsibility. However, more important than the amount of their responsibility is how well they perform it—more important than their authority is their ability to apply it.

### How much can you save with the isocracking process?

J. W. Scott, J. A. Robbers, N. J. Paterson and H. M. Lavender, April 1960

This article provides material balances for typical refineries converting middle distillate to gasoline. These cases demonstrate the advantages of the isocracking process for control of product distribution and quality.

### When metals poison cracking catalyst

E. C. Gossett, June 1960

This article is an investigation of the effect of poisons on fluid catalytic cracking yields. It details how the hydrogen producing factor can be used as a criterion for operating a commercial unit and provide a measure for selecting feedstocks and determining catalyst replacement rates.

### Mechanical specification of trays

H. C. Glitsch, August 1960

Mechanical aspects of tray specification are as important as the process itself. After chemical process and metallurgical specifications have been drawn, the tray must be mechanically designed to meet these specifications. This article provides an analysis of the items to cover when specifying fractionation trays.

### Which to use—Relief valve or rupture disc?

P. A. Puleo, October 1960

The main difference between a relief valve and rupture disc is obvious—one will reseal and the other will not. The questions are: Where to use one or the other and when to use both? What system factors affecting disc and valve perfor-

mance should be considered? What problems inherent in the services themselves should be considered (i.e., leakage, pressure limitations and settings, capacity, among others)?

### Which acetylene feed is best?

D. C. Lockwood, November 1960

This article compares the effect of methane, ethane and propane on overall manufacturing costs. The effect of fuel, oxygen and investment costs for various paraffin feeds are thoroughly discussed.

### To engineering contractors: A checklist for project engineers

February 1961

Checklists can resolve many questions about a project in the shortest time. One of the most important lists in Phase 1 (the pre-contract stage) is the construction questionnaire. This article provides questions that should be answered about the construction site.

### New uses spark propylene growth

T. C. Ponder, March 1961

Propylene, one of the first petroleum raw materials used in chemical manufacturing, is being studied by petrochemical manufacturers as though it were a new discovery. This exciting new look at propylene is due to the development of several new processes into commercial production. This trend can mean increasing demand for high-purity propylene.

### Design tips for refinery tank farms

A. H. Younger, July 1961

Three variables control the design of refinery storage tanks, pumps and miscellaneous items: crude yields, sales estimates and refinery production forecasts.

This article shows how these variables are predicted, along with detailed examples on the design of storage tanks and accessories.

### Don't be confused by rotary pump curves

A. A. Zalis, September 1961

Some engineers throw up their hands in despair when a screw or gear pump operates at viscosities other than those shown on pump curves. This article provides a simple way to extrapolate rotary pump curves and find operating characteristics at other viscosities.

### For ethylene oxide, it is uphill for the second billion

J. Gordon, October 1961

Process improvements and aggressive development of new markets point to steady growth for ethylene oxide on its way to 2 Blb/yr.

### Is epoxidation in your future?

J. Gordon, April 1962

Epoxidation is in your future if you are interested in plastics and plasticizers made from abundant and low-cost materials. Major growth in epoxidation may be attributed to improved processing techniques, greater variety and quality of products.

### Comparing cooling towers: European vs. U.S.

J. W. Hubenthal, June 1962

Industrial expansion globally has been witnessed within the cooling tower sector. This article provides a comparison of fundamental differences in cooling tower design between the U.S. and Western Europe.

### Now—Make jet fuel from coal

M. Letort, July 1962

Jet fuel can now be made from coal using established catalysts and hydrogenation techniques. Ample supplies of coal tar fractions offer an additional source for high-energy jet fuels.

### Management's role in the creative 'climate'

A. Wintringham, October 1962

This work details what management can do to set up a good corporate climate for encouraging and using the creative potential of engineers and how to develop young engineers along creative lines.

### Polymethylbenzenes go commercial

L. T. Eby and P. E. Neman, March 1963

Five C<sub>9</sub>–C<sub>10</sub> aromatics have reached the commercial market. Following cumene, pseudocumene, naphthalene, mesitylene and durene are more alkyl-substituted benzenes reaching for commercial status.

### Make resins from styrene-butadiene

I. A. Eldib, June 1963

Now resins from styrene-butadiene can be made using sodium catalyst or emulsion copolymerization. This article provides data on costs, raw materials and process variables, together with uses and applications.

### Which steel for refinery service?

C. H. Samans, November 1963

This article describes selection and evaluation of carbon steel, ferritic stainless steel and austenitic stainless steel for refinery service above 650°F.

### How to evaluate contract maintenance bids

H. D. Dobe, January 1964

In this article, the author suggests two checklists: One to evaluate eligible contractors and the other on precontract information to the bidders. Some of the items discussed include:

- Whom do you invite to bid?
- How do you select the contractor?
- Conference vs. solitary briefings to bidders
- Annual vs. as-needed contracts
- Types of contracts.

### Better lab practices in chromatography

J. Q. Walker, April 1964

These hints will help you make your chromatographic equipment safer, faster and more productive. They include tips on filament and fire protection, carrier gas purification, optimum column and temperature control, better pressure control and reorder operation.

### What's optimum exchanger pressure drop?

F. W. Lohrisch, June 1964

There is an optimum pressure drop in every heat exchanger at which the purchase price plus the operating costs are reduced to a minimum. Increasing fluid velocities increase heat transfer and pressure drop and lower the purchase price but increase pumping power requirements. What is optimum? This article provides equations and nomographs that consider physical properties of the fluid, purchase price of the exchanger, working hours, power costs, etc., to find the optimum pressure drop for a particular exchanger.

### Practical design of flare stacks

G. R. Kent, August 1964

A key factor in flare stack design is in the escape time for personnel assumed to be at the stack base at the time of ignition. In this article, a basis is provided to limit the maximum heat radiation at the stack base. The effect of flame characteristics, gas flow, escape time, heat radiation and wind on stack diameter and height are covered in this design method.

### Cut heat costs with chemical cleaning

J. H. VanSandt, December 1964

This case history shows that a refinery can cut fuel costs by \$250,000/yr by picking up an additional degree of temperature in all its heat exchangers. Types of exchanger deposits are described together with techniques for removing them chemically, along with steps in chemical cleaning.

### Petrochemicals: Big drive in '65

F. G. Sawyer, January 1965

With the usual ups and downs, and certain petrochemicals dragging, overall production, sales and capacity utilization look for the best year yet in 1965.

### How to reduce hydrogen plant corrosion

K. L. Moore and D. B. Bird, May 1965

High temperature and wet carbon dioxide (CO<sub>2</sub>) were the major causes of corrosion in a U.S. hydrogen plant. Here are the details of how the problems were solved. Subjects discussed include Incoloy furnace tube corrosion from residual welding slag, high-temperature overstress and thermal fatigue, wet CO<sub>2</sub> corrosion, chloride stress corrosion cracking of stainless steel in MEA service, hydrogen attack and denickelification of monel condenser tubes.



### Camel LNG plant: World's largest

C. G. Filstead, July 1965

The third liquefaction line is now in operation at Arzew, Algeria. It is the world's first commercial scheme to liquefy natural gas for export. Here is how it is operating.

### Design criteria for large urea plants

L. H. Cook, February 1966

A 1,500-metric tpd, single-train urea plant is now economically feasible. This article provides criteria for optimum design.

### New catalyst for Sohio process

What's HapPenIng, June 1966

The Standard Oil Co. (Ohio) will begin construction in the spring of 1966 on a plant in Lima, Ohio, to produce a new, alternative catalyst to be used in Sohio's acrylonitrile process. Commissioning is scheduled for early 1967.

### What's the future for PVC?

G. Olivier, September 1966

Because it is so well established in the thermoplastic field, polyvinyl chloride should have an annual growth rate during the next 10 yr more than 12%.

### Essential information for piping design

R. W. Judson, October 1966

Three major source documents are essential for good piping design: engineering flow diagrams, nomenclature and equipment elevations. This article explains each in detail, providing content and source of these essential documents.

### "Clipping Method" for turnaround scheduling

C. K. Gimlin, January 1967

Job sequences are compiled on a written work order. Then, jobs for each craft are "clipped" from the work order and placed in job folders. These are transferred to a daily work schedule for each craft. As the turnaround progresses, changes in work requirements can be quickly rescheduled using the system.

### How to handle a safety inspection

V. J. Whitehorn and H. W. Brown, April 1967

Periodic inspections are a key part of a good safety and fire protection program. This article provides a checklist to help personnel ensure their plant is getting the attention it needs.

### Less sulfur in the air from fuels?

R. C. Mallatt, December 1967

Although the use of petroleum and natural gas fuels is growing, there is less air pollution from the sulfur in these fuels. In the U.S., investments in processes which desulfurize have reached approximately \$700 MM, according to a recent industry survey.

### Learn about analog computers

T. W. Cadman and T. G. Smith, February 1968

This series describes the basic concepts of analog computers. It will detail how analog computers can be used to simulate processes and to solve problems peculiar to the HPI. Among the items to be covered include amplitude scaling, time scal-

ing, process simulation, circuit design, diode switching, function generation, memory and logic, and future roles.

### Noise pollution: A new problem

J. M. Hopkins and R. H. Congelliere, May 1968

Air and water pollution have stirred a new interest—noise pollution. This article discusses the effect of excess noise on employees, existing legislation designed to control industrial noise and an effective noise-control program.

### Compare DGA and MEA sweetening methods

J. C. Dingman and T. F. Moore, July 1968

Among the processes for sweetening natural gas, monoethanolamine (MEA) ranks at or near the top in number of commercial installations. Now, a very similar process, using a chemical called diglycolamine (DGA), presents credentials which appear to make it extremely competitive with the long established MEA process.

### Petrochemicals: Still fine in '69

F. G. Sawyer, January 1969

Petrochemicals remain the pacesetters of the HPI. Last year proved better than expected, but the same problems of price fatigue and overcapacity plagued certain areas. Discounting short-term variations, the long-term outlook is excellent.

### Optimum: Hydrocrack + reform

J. R. Kittrell, G. E. Langlois and J. W. Scott, May 1969

For best refining operations, it is important to consider the yield-octane relationship between hydrocracking and modern catalytic reforming. This article provides some generalized correlations.

### Olefins by dehydrogenation-extraction

D. B. Broughton and R. C. Berg, June 1969

By combining catalytic dehydrogenation of linear paraffins with molecular sieve extraction, high-purity linear internal mono-olefins are produced in good yield at a cost of approximately \$0.02/lb.

### Furnace tubes: How hot?

J. M. Lenoir, October 1969

The measurement of surface temperatures for furnace tubes is important to achieve optimum operation. Not hot enough: Uneconomical processing; too hot: Quicker tube failures.

### Ideas for gas plant automation

B. A. Eckerson, December 1969

This article provides a look beyond the control of simple operating variables. It provides practical ideas—many already tested—for the control of air coolers, sulfur plants, plant emergencies, truck loading and the operation of absorption oil units. **HP**

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## Sustainable refinery of the future: Versatile, efficient and smart

Greenhouse gas (GHG) emissions occur alongside an inflection point for global refined product consumption. Since the 1850s—when the first oil refineries were constructed—the world has changed dramatically as refined product demand has continued inexorably upward. This assumption is no longer valid as refined product demand has little to no incremental growth beyond its pre-pandemic COVID-19 level.

During COVID-19, the International Energy Agency (IEA) reported global demand for crude oil decreased by about 30%, which is a decrease of 30 MMbpd. A significant reduction in the crude oil demand was a direct result of the mobility restrictions during the pandemic and heavily impacted the petroleum industry. Furthermore, the increasing demand for clean fuel consumption and the growing electric and hybrid vehicles market contributed to the decrease of conventional fuels production.

Today, 80% of each oil barrel is used to make fuels, while the rest is converted into petrochemical products. Facing the global market challenges, the refining industry is encouraged to look for alternatives that ensure its survival and sustainability. Better integration between refining and petrochemical production processes may be a solution to the challenge. Based on the latest trend of increased green fuels production, it is estimated that fuel production tendencies will shift towards increased production of chemicals, which is estimated to double by 2030. The focus on the closer integration between refining and petrochemical industries is to enhance the synergies of the existing opportunities between both sectors to generate value to the entire crude oil production chain.

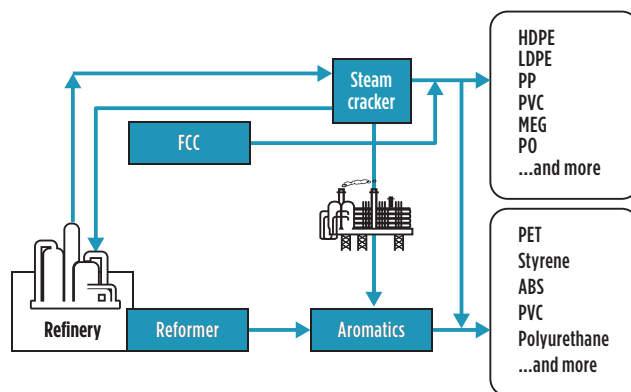
The technological base of the refining and petrochemical industries is similar and may lead to cooperation possibilities to reduce operational costs and provide additional value to derivatives production at refineries, considering that the petrochemical industry has been growing at a higher rate when compared to the transportation fuels market. It is less environmentally aggressive compared to the crude oil derivatives produced by the petroleum industry. The integration potential and the synergy among the processes rely on the refining production scheme adopted by the refinery and the consumer's market. Secondary process units, such as catalytic cracking and catalytic reforming, can be optimized to produce petrochemical intermediates of streams incorporated into chemical pool production.

**Moving to clean energy.** Extensive hydrogen production by the petrochemical industry may be considered an excellent al-

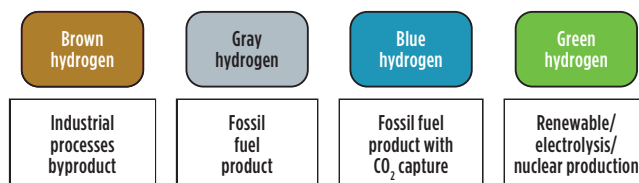
ternative to conventional fuels like gasoline, diesel and fuel oil produced by the refining industry. Green hydrogen is generated by renewable energy or from low-carbon power. Green hydrogen has considerably low carbon emissions, but the high cost of its production is the main factor behind its minimal usage.

The petrochemical industry is one of the biggest consumers and producers of hydrogen. Beyond its preferred use as a raw material, hydrogen can also be used to replace natural gas used as fuel for furnaces since natural gas/hydrogen mixtures release less carbon dioxide (CO<sub>2</sub>) when combusted. As a result, hydrogen may play an essential role in the decarbonization of the petroleum and petrochemicals industries, considering its cost-competitiveness and it being produced from emissions-free production processes.

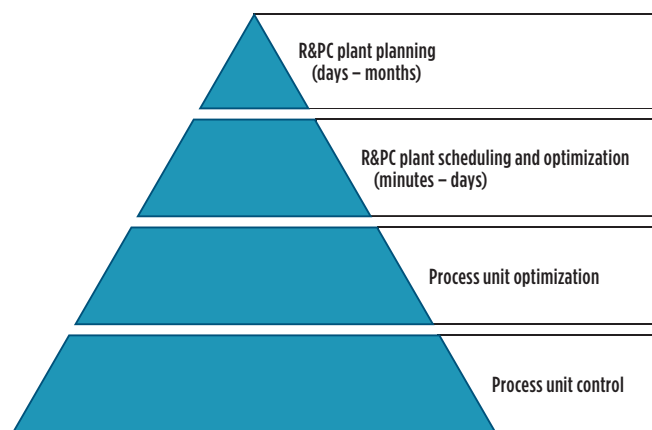
Projects that contribute to climate targets and demonstrate low-carbon technology innovation are highly prioritized by European Union (EU) innovation funds and government grant programs. For example, the EU Innovation Fund ap-



**FIG. 1.** Standard approach of petroleum and petrochemical industry integration.



**FIG. 2.** Hydrogen production classification.



**FIG. 3.** Planning and scheduling of AI dynamic optimization package based on the neural network model.

proved an €88-MM grant to Neste's green hydrogen and CO<sub>2</sub> capture and storage (CCS) project. This project aims to reduce GHG emissions quickly and efficiently at the Porvoo refinery in Finland. This transformation project will enable the Porvoo refinery to significantly decrease CO<sub>2</sub> emissions by approximately 4 MMtpy. The reduction in emissions will be achieved through CCS by electrolysis solutions, enabling the decarbonization of production at the refinery.

**Increased efficiency.** To maintain sustainable profitability, petroleum and petrochemical industries must quickly respond to changing market conditions by switching from producing one product to another. The raw material for gasoline production may be redirected to petrochemicals feedstock production that gains a higher price, and back again when prices fall. Production efficiency—the capital value of industrial production—is defined by how efficiently it uses critical resources to capture growth. The efficiency measurement is defined by how effectively a refinery uses:

- Level of emissions
- Produced water
- Carbon and the components of hydrocarbons
- Hydrogen
- Utilities.

These efficiencies are balanced by the refinery's overall business strategies, which may help determine the effective use of capital value. Utility efficiency represents how effectively the energy is used to operate the refinery. For example, the efficiency of water—used to regulate temperatures in the refinery—is considered a critical factor because it is almost always scarce and requires many resources for its operation and cleaning.

Due to sustainability efforts and increased complexity, refineries are facing the challenge of increased volume data and material flow over the processing and distribution. The advent of the Industry 4.0 initiative and modern artificial intelligence (AI) with machine-learning tools open new horizons towards industrial digitalization by enabling automated procedures and communication by means that were previously unavailable. The technology seen in the context of Industry 4.0 aims to reduce the complexity of these systems. Efficient management of the substantial amounts of generated data and increased

number of variables requires integration of sophisticated and advanced tools. Industry 4.0 developed data and information from various sources and levels that can be integrated into methods and systems for adaptive and effective decision-making must be further analyzed to manage the various and conflicting decision variables.

AI solutions may play an essential role in achieving sustainable development for sustainable production, pollution control, water efficiency, industrial safety, clean air and healthcare. These advanced digital application solutions integrate real-time data and advanced analytics for better decision-making, underpinning applications that can dramatically improve process control behavior, efficiency and sustainability.<sup>1–6</sup>

**Modcon-AI solution.** Corrective actions based on AI technology can improve operational reliability, increase process optimization, optimize energy consumption, reduce waste and emissions and improve water utilization. Enhancing the capabilities of plant operators can close the gaps related to operation experience caused by personnel attrition.

Big data analysis functionality includes multidimensional fusion and distribution of incoming data, abnormality of novel events detection, clustering, decision trees, linear, polynomial, logistic regression and escalation of real-time novelty analysis using deep learning technologies.

Investment in AI and machine-learning techniques enable the sustainable development of the modern petroleum and petrochemical integrated industry by adopting business strategies and developing artificial solutions that meet the needs of the enterprise, while protecting, sustaining and enhancing the human and natural resources needed in the future. **HP**

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## Managing complexity in engineering and construction projects

It is widely accepted that new management methods are needed to curb the frequent delays and cost overruns observed in engineering and construction projects. New approaches, such as the Last Planner system of production control and advanced construction packages, can help to increase construction efficiencies; however, none of them address the root causes of problems, which is the difficulty of managing the inherent complexities of large engineering and construction projects.

This article highlights the deficiencies of today's working practices and proposes a practical method to manage complexity.

**The failure of conventional project management.** Numerous surveys conducted in recent years have shown that conventional management methodologies are incapable of avoiding schedule and cost overruns in engineering and construction projects. A macro survey conducted by Ernst & Young (EY) on 365 oil and gas projects revealed that 65% had long delays, 78% had suffered significant cost deviations, and the average budget overrun was 53%.<sup>1</sup>

For some time, it was thought that tools such as 3D computer-aided design and building information modeling would solve the problem; however, while they have contributed to substantial improvements in safety and technical quality, their impact on cost and schedule has not been very significant.

The first attempt to abandon the traditional project management approach was made by Glenn Ballard and Gregory Howell in the 1990s when they developed the

Last Planner methodology. In essence, they applied lean management concepts developed by Toyota. Inspired by the “pull” principle—which states that things must be done “when and as required by the last links in the project chain”—and under the conviction that the detailed initial schedule is always totally wrong, they proposed to start with a simple master schedule and to leave the detailed planning to the construction foremen.

While the Last Planner methodology is widely used by building and civil works contractors, it has had little success on oil and gas projects. The reason could be that oil and gas projects involve multiple contractors—therefore, it is very difficult to obtain timely feedback from construction foremen.

Information technology (IT) and new product development projects have already abandoned the traditional management approach. A group of software developers launched the Agile Manifesto for software development in 2001, which implies a total departure from conventional project practices. Today, these software developers use methodologies such as Scrum, which does not have an overall schedule. Instead, the project is divided into sequential steps of no more than 4 wk. The final scope is frequently redefined, and the contractual relations are totally flexible. This approach has been so successful that many wonder why our industry does not apply it to engineering, procurement and construction (EPC) projects. The primary reason is that oil and gas EPC projects are drastically different. The problem encountered in IT projects is that the objective is not entirely

defined, and the design specifications are few or totally nonexistent. Conversely, in EPC projects, the objective for the final product is clear from the beginning, and the volume of design codes and specifications is overwhelming.

The last divergence from conventional project management is the Advanced Work Packaging (AWP) methodology, which was co-developed by the Construction Industry Institute (CII) and the Construction Owners Association of Alberta (COAA) in Canada. These organizations found that the average hands-on-tools time for construction personnel is below 37%, and that the rest of their time is wasted in document/material searches or from idleness. To try to solve this challenge, the researchers proposed a procedure based on dividing the construction work into packages and transferring the responsibility for planning to the field. Instead of leaving it to the foremen, as the Last Planner system does, they employ specialized construction planners. Each week, the planners prepare the packages that are fully ready for execution and deliver them to the foremen. Additionally, to enforce a construction-driven design and an orderly delivery of information and materials, engineering disciplines are required to prepare a separate information package for each of the construction packages.

According to the CII, this method can lead to improvements of up to 25% in time-on-tools efforts for construction labor. Depending on the type of project and geographic area, this would represent savings of approximately 5% of the total project cost. This is an impressive savings, but it



is not enough to drive away the two-figure deviations found in many EPC projects.

The authors' thesis is that the main cause of cost and schedule overruns is the intrinsic complexity of EPC projects; therefore, the problem will only be solved when the industry finds a way to effectively manage that complexity.

**The roots of the problem.** The causes of EPC deviations most frequently mentioned in literature include the following:

- Client design changes
- Low construction productivity
- Aggressive bidding
- Poor project planning and scheduling
- Financing problems
- Slow decision-making
- Acts of God.

If these deviations are analyzed, the underlying cause is the complexity of EPC projects. In theory, client design changes should not be harmful because the contractor will be compensated, and the client only makes them if the benefit/cost ratio is positive. If changes end up being a problem, it is because their impact turns out to be worse than expected. The reason this happens so often is that project complexity makes it difficult to foresee the real impact of the changes. It also makes it very difficult to reach an equitable agreement between the parties on the costs of the change.

The second deviation—low construction productivity—is not due to lack of experience of construction personnel, but to problems caused by delays in the delivery of drawings and installation materials. The complexity of the project should be the only reason for highly experienced engineering and procurement teams to end up doing a bad job.

The third cause is aggressive bidding. Market pressures can often force contractors to provide low prices, but the complexity of EPC projects means that, even unintentionally, bids can easily be unrealistically high or dangerously low.

Complexity plays an important role in all the deviations, including Acts of God, because risk analysis and mitigation measures are always carried out before starting a project. If they prove to be insufficient, it is because the complexity of the project makes it very difficult to gauge the consequences of the acts.

While there are other factors that can also lead to project failure, complexity is

by far the most common and most difficult to manage. In addition, complexity is aggravated by the urgency of capital projects. Project lead times are excessively long for an increasingly dynamic economy, and this makes urgency present at every step of the project. This urgency exacerbates the consequences of complexity because, in addition to limiting the time available to try to untangle the complexities of a project, urgency often forces the design to move forward based on assumptions rather than on firm data.

Academic research supports the conclusions drawn in this article. After a systematic analysis of 86 research papers on the causes of project failures, Denicol *et al.*<sup>2</sup> found that the dimensions that make megaprojects so difficult to manage include size, uncertainty, complexity, urgency and institutional structure.

There are numerous research papers on the origin of project complexity, but, in the case of EPC projects, one only needs to see the detailed critical path method (CPM) and program evaluation and review technique (PERT) network to understand where this complexity comes from. A medium-sized EPC project can easily have more than 20,000 tasks, with a much higher number of interactions or dependencies among them. Like trees that obscure the forest, complexities blur and hide problems, and, without a clear vision, it is very difficult to manage them.

Prieto<sup>3</sup> said that, in addition to obscuring the problems, complexity amplifies even the smallest and seemingly improbable risks. In his book, *The Improbability Principle—Why Coincidences, Miracles and Rare Events Happen Every Day*, David J. Hand mathematically describes the amplification mechanisms, such as Lorenz's butterfly effect. The following will show that the size and complexity of this maze of multidisciplinary tasks and interactions are further aggravated by the limitations of the tools used to visualize this maze.

**The schedule problem.** Scheduling is a key tool for efficiently planning and controlling the project's execution. One might think that the schedule's function is limited to controlling execution times, but scheduling also has a strong impact on many other factors—such as spent worker hours, the amount of rework required, construction efficiency, the necessary volume of surplus materials, and many other cost ele-

ments that are affected by the schedule design. The following are several examples:

- If the design of cable routings is started with immature information, designers will have difficulties obtaining the data they need and spent worker hours will increase. Furthermore, they may have to work on assumptions, which may, in turn, lead to a wave of redesigns in downstream disciplines—including construction reworks—when the correct data arrives.
- If construction subcontractors are mobilized too early, they will suffer from drawing shortages, leading to a drop in efficiency.
- If time frames assigned to procurement and subcontracting tasks are too short, chances are that there will not be enough time to get the most competitive prices.
- If the initial schedule is too optimistic, the project will accumulate delays, often leading to staff demotivation.

The schedule is, therefore, the most powerful tool available to project management. The budget is an essential reference for cost control, but it is only a reference and not a mechanism that can act directly on costs.

There are very powerful schedule management tools on the market. While they are designed to display a myriad of activities, with the ability to drill down into the details, they do not provide an all-encompassing vision of project structure. These tools cannot produce clear summaries capable of communicating the complex task networks and the roles of the interactions between them.

Managing a project without a clear overall vision of its structure is like driving a car in the fog. There must be a clear overall picture to enable the EPC contractor to detect risks and opportunities, measure the consequences of decisions on downstream activities, and choose the best implementation strategies.

**Mapping of project interactions.** There are few solutions available to obtain a clear overview needed to manage large, complex projects. If these solutions are simple tools and are not complicated systems that add more complexity to the already overloaded project management environment, then advanced analytics can help.

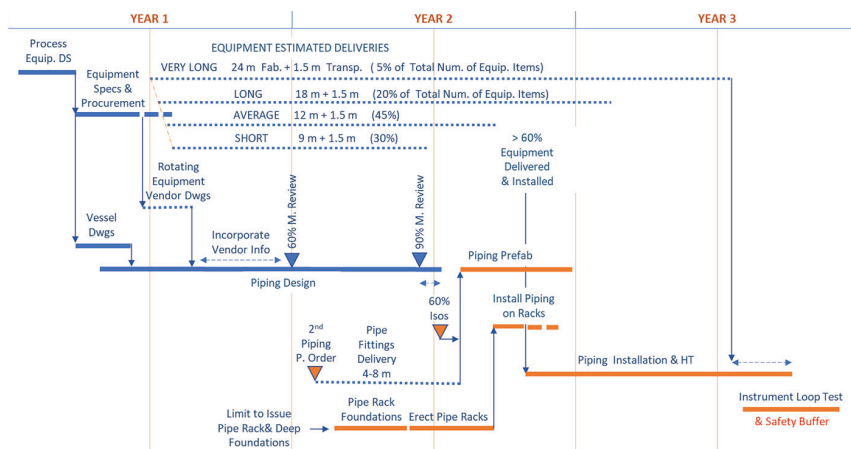


FIG. 1. Simplified project interactions map.

One possibility is the use of simplified schedule representations. By grouping common tasks, one can draw a map or a network showing the essential groups and their main interactions. A simplified project interactions map is shown in FIG. 1. This mapping should be sufficiently detailed to shed light on execution strategy decisions—including obstacles to overcome to advance equipment inquiries, prioritization of equipment procurement, identification of areas where value engineering exercises should be performed, modularization, and conditions for mobilization of construction subcontractors, among others.

The first time the map is prepared, this task can be very laborious, requiring the involvement of all project disciplines, especially construction. However, once the first one has been drawn up, it is very easy to adapt it to each new project.

During the launching of a new job, the map is used by the management team to decide the primary execution strategies. Once these strategies have been determined and reflected in the map, it can be used as a guide for schedulers in the development of the initial detailed schedule. In addition to improving the reliability of the schedule, this map drastically reduces the time required to complete it.

After the detailed schedule has been issued, daily work is controlled by it. However, it is advisable to keep the map alive and updated throughout the life of the project, both for its usefulness for decision-making and also to incorporate lessons learned that may be useful in future occasions.

The authors have called these documents “interaction” maps to stress the importance of interactions or dependencies

between tasks. A mere change in a dependency can transform a project. For example, if starting the civil design of a process area after receiving 90% of the vendor’s drawings (projects are typically started with 60% of the vendor’s drawings), the project will be completely different. Civil works may start earlier, but there will be more drawing revisions, more site reworks and more change orders.

While tasks and durations are clearly shown in multiple project documents, dependencies are practically ignored. Project schedulers use them to build the PERT-CPM network, but they do not bother to give them much publicity because they realize that few people will take the time to review them. Moreover, the arrows used to represent them tend to get very intricate, and there is no easy way to reflect them in project reports. Since dependencies receive little attention, there is very little knowledge about their impact on project results. This is a major problem because the art of planning is the art of wisely selecting dependencies. **HP**

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## Considerations for not providing a dedicated spare pressure-relief device

Pressure-relief devices (PRDs) play a critical role in the hydrocarbon processing industry. They act as the last line of defense in protecting plant equipment from overpressure and are mandated by the American Society of Mechanical Engineers (ASME). This article provides some key factors that process engineers and plant operators must consider to determine if an installed spare PRD is necessary.

Like many other plant components, relief devices require routine maintenance to ensure safe and reliable plant operation. While most of the PRDs in hydrocarbon processing plants can be taken out for maintenance during plant turnarounds, certain PRDs may require more frequent maintenance while the plant is in operation (onstream). The term “onstream” refers to the overall plant operation. Reasons for more frequent maintenance could be due to safety requirements or possibly because the PRD is installed in a fluid service where fouling, corrosion or plugging could potentially impact PRD operation.

Onstream maintenance of a specific PRD in the plant can be achieved by one of the following options:

1. Providing an alternate and adequate relief protection to the protected equipment (e.g., a spare PRD, or an alternate and adequate flow path to another PRD)
2. Isolating, draining and depressurizing the protected equipment from all possible overpressure sources (taking the equipment out of service)
3. Eliminating as many overpressure sources as feasible, and implementing administrative controls for monitoring the protected equipment for the duration of the PRD maintenance.

Process engineers are required to review these options during the front-end design development step, with input from the plant operations team, to make an appropriate decision. PRDs requiring onstream maintenance are, in general, provided with isolation valves on inlet and outlet (if applicable) pipelines. ASME code requires administrative controls to be in place for proper operation of the isolation valves in the relief path so the equipment’s overpressure protection is not compromised. These requirements include providing locks or car seals in addition to administrative controls to prevent accidental closure (for more information, refer to ASME BPVC Section XIII Non-Mandatory Appendix B). Process engineers and plant operators must be familiar with the ASME code re-

quirements, and Appendix B provides valuable guidance and requirements for determining a need for installing a dedicated spare PRD. The following will review the three options in further detail.

**Option 1.** Providing an installed spare PRD is generally a preferred way to provide adequate overpressure protection to the process equipment. While this option involves initial capital expenditure for the PRD and associated piping, it also provides the safest way to keep the protected equipment in continuous operation for the duration of the maintenance. Plant operators are required to follow stringent administrative procedures for isolating the PRD requiring maintenance.

In the absence of an installed spare PRD, there can be other creative ways to achieve the same purpose. This includes utilizing PRDs on nearby equipment to provide the necessary protection by means of utilizing an existing pipe routing for a temporary relief path. However, process engineers should perform a thorough analysis to ensure that such a temporary and alternate relief path is adequate in terms of hydraulic requirements (inlet pipe pressure loss), PRD flow area and fluid service compatibility.

**Option 2.** This option is best suited for equipment that can be taken out of service while onstream plant production is maintained. A spare PRD may not be required if the entire protected system can be isolated during normal plant operation. Equipment operating in intermittent service also may not require a spare PRD. For example, consider a hydrocarbon system containing multiple catalyst bed vessels in parallel, where at least one vessel is always isolated for catalyst regeneration and is in standby mode for a prolonged duration. A spare PRD may not be provided for protecting such vessels, as maintenance can be performed when the vessel is in standby mode. In such cases, the duration of the maintenance should be given careful consideration, as the vessel cannot be returned to service without code-compliant relief protection. Plant operators generally rely on administrative procedures to open and close several valves for placing equipment back in service. Failure to properly follow these administrative procedures can compromise the overpressure protection mandated by the ASME code. One such safety incident was the ruptured heat exchang-

er in June 2008 that killed one worker and injured six others at the Goodyear Tire and Rubber Co. in Houston, Texas.<sup>1</sup> One of

PRDs requiring onstream maintenance are, in general, provided with isolation valves on inlet and outlet (if applicable) pipelines. ASME code requires administrative controls to be in place for proper operation of the isolation valves in the relief path so the equipment's overpressure protection is not compromised.

the root causes of this accident was failure to properly follow the procedure of opening the PRD inlet piping isolation valve before placing the heat exchanger into service.

**Option 3.** This is the least preferred option, as it involves operating the process equipment without overpressure protection under administrative controls. One of the first things that the plant operator is required to do in this option is to identify all potential overpressure sources beforehand and attempt to eliminate or minimize the likelihood of overpressure from such sources for the duration of the PRD maintenance. In this option, assuming that there are isolation valves in place, the PRD must be first isolated by closing the inlet and outlet isolation valves before the maintenance can begin. Closure of the isolation valves would lead to blocking the relief path and to operating the protected equipment with a risk of overpressure. Plant operators are required to stay in compliance with the ASME code for proper implementation of administrative controls. ASME BPVC-XIII Appendix B-7(d) states:

“Procedures are in place to provide pressure relief protection during the time when the system is isolated from its pressure relief path. These procedures should ensure that, when the system is isolated from its pressure relief path, an authorized person should continuously monitor the pressure conditions of the vessel and should be capable of responding promptly with documented, pre-defined actions, either stopping the source of overpressure or opening alternative means of pressure relief. This authorized person should be dedicated to this task and should have no other duties when performing this task.”

Plant operators should consider several factors to safely rely on administrative controls for monitoring unprotected equipment. One such factor is the duration of maintenance. Can the relief device be returned to service in a reasonable amount of time? Another factor is training. What kind of training would be required for authorized persons to respond promptly in an event of pressure excursion in the process service? If possible, process engineers and plant operators should steer away from this option, as this involves several factors that cannot be fully accounted for during the plant design.

**Multiple overpressure scenarios.** There can be more than one overpressure scenario that is applicable for a PRD. Over-

pressure due to an external pool fire is a well-known scenario that is applicable for process equipment at grade level. Additional overpressure scenarios include blocked outlets and auto-control failures, among others (see API 521 for more information). The process engineer should review all applicable overpressure scenarios when determining the need for a spare PRD.

It is a generally accepted industry practice not to provide spare PRDs in the following applications, as the PRD maintenance interval typically aligns with the protected system maintenance interval:

- PRDs installed exclusively for protecting equipment from external fire (fire-only PRD)
- PRDs installed in cooling water service exclusively for protecting the equipment from thermal expansion (cooling water thermal).

**Multiple PRDs.** Multiple PRDs are often provided when a single PRD is not adequate to handle the required relief flow-rate. The ASME code allows staggering the PRD set pressures in this case. For multiple PRDs:

- A single spare PRD may be installed with the basis that administrative controls are in place to perform maintenance on one PRD at a time. When a single spare PRD is installed, performing maintenance on multiple PRDs would result in inadequate relief protection, which is a possible code violation.
- The spare PRD should have an orifice flow area identical to the operating PRD with the largest area.
- When the spare PRD is put into operation, at least one PRD should have a set pressure at 100% of the maximum allowable working pressure.

**Takeaway.** The ASME code does not mandate installing a spare PRD. However, in the absence of an alternate and adequate relief path, the ASME code mandates the implementation of proper administrative controls for safe isolation and subsequent monitoring of the protected system for the duration of PRD maintenance. Administrative controls play a critical role in the safe operation of any plant, and many plant operators prefer to install a spare PRD to provide an adequate and equivalent overpressure protection. Process engineers and plant operators must be conversant with the applicable regulatory requirements and must review all PRDs on a case-by-case basis for determining whether an installed spare PRD is, or is not, necessary. **HP**

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- <sup>2</sup> ASME Boiler and Pressure Vessel Code, Section XIII-2021, “Rules for overpressure protection.”

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## Preferential baffle reboiler—Part 2

Distillation towers consume ~30% of the energy in a refinery or petrochemical facility. The reboiler is the stomach of the distillation tower that consumes the energy to separate the components. Any improvement in design or operational flexibility will save the energy and profitability of the plant. Two main types of reboilers are in use: a circulating (conventional) reboiler and a once-through reboiler.

Part 1 of this article,<sup>1</sup> which delivered a brief introduction of the preferential baffle reboiler and its working principle, was published in the April issue. If designed accurately, a preferential baffle reboiler (baffle with hole) or baffle with underflow can provide benefits; otherwise, it can show detrimental effects.

Part 2 will describe the design of the preferential baffle reboiler with the help of hole size, shape of the hole, and elevation of the hole in the baffle. It also provides recommendations and guidelines for optimum design. In this type of preferential baffle reboiler, the elevation, shape and diameter of the hole are all important.

**Design and performance.** A thermosiphon reboiler's performance is affected by many factors, including the diameter of inlet and outlet piping, elevation of a column, length of pipelines, Delta T ( $\Delta T$ ), driving force (liquid head), etc.<sup>2</sup> All factors are fixed and considered during the design phase, except the head of the liquid, which may vary based on the level in the column bottom sump. If the level drops below a certain point, the head of the liquid is reduced and will be unable to push the effluent of the reboiler into the column. In this scenario, the reboiler reduces the circulation (or thermo-siphoning) effect, but heat input to the reboiler continues. This creates over-vaporization of lighters and may cause polymerization issues or an accumulation of heavies in the reboiler. Even if the head is maintained

and the reboiler is heated sufficiently, the accumulated heavies resist further circulation through the reboiler and degrade the thermosiphoning effect.<sup>3-9</sup>

**Location of the hole.** Part 1 mentioned that the flow of the liquid through this baffle hole should be unidirectional to make it a preferential reboiler. The head of the liquid and the height of the skirt support of the column from the reboiler elevation are responsible for thermosiphoning (sending a mixture of liquid and vapor into the column without any pump). Therefore, the location of the hole in the baffle should be higher than the level of the liquid required to run the reboiler or to circulate liquid through the reboiler with the thermosiphoning effect (FIG. 5).

The driving force is equal to the resistance force against the flow (Eq. 1):

$$DP_{driving} = DP_{inlet} + DP_{outlet} + DP_{reboiler} + DP_{two-phase} \quad (1)$$

where:

$DP_{inlet}$  includes friction losses of inlet line and entry loss, and  $DP_{driving}$  is equal to  $H^* \text{density}$

$DP_{outlet}$  includes friction losses of outlet line and exit losses

$DP_{two-phase}$  is dual-phase losses, and is equal to  $Hr^* \text{mixed-phase density}$

$DP_{reboiler}$  is the exchanger losses.

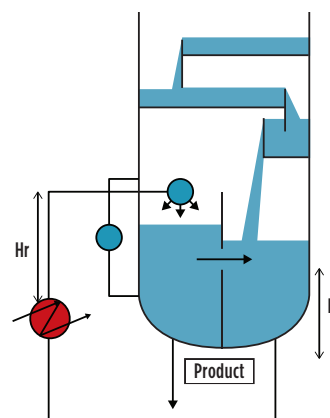
Many plants make a hole at the bottom of the baffle. This may cause head loss if an excess amount of product is withdrawn from the product compartment and the level in the reboiler compartment is reduced. It can also starve the reboiler of liquid (FIG. 6). Another problem with the hole at the bottom of the baffle is that unheated liquid (bottom tray liquid) can enter directly into the product compartment without going through a reboiler, which would contain lighters and may result in off-spec product. This diminishes the efficiency of the distillation column. Many

operators run the tower at a high bottom temperature to increase efficiency; this negatively affects the reboiler as well as the tower's productivity.

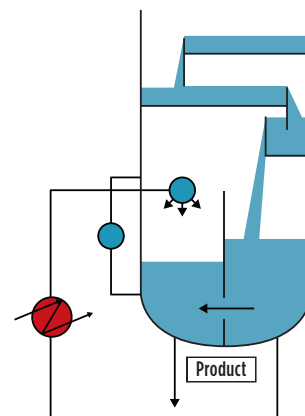
**Shape of the opening (hole).** In some plants, the shape of the hole in the baffle

**TABLE 1.** Discharge coefficient of different shapes

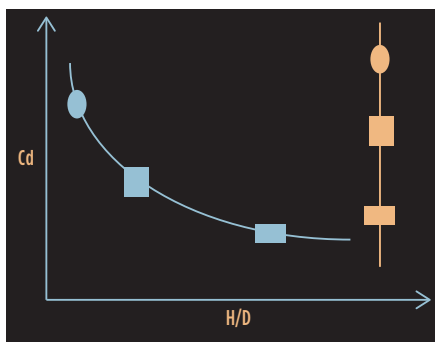
Shape	Circular	Square	Rectangular
Discharge coefficient (Cd)	High	Low	Very low



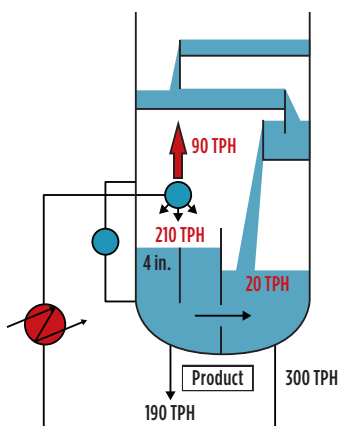
**FIG. 5.** Ideal elevation of hole.



**FIG. 6.** Hole at bottom of baffle.



**FIG. 7.** Cd of different shapes—the Cd reduces with diameter and head.

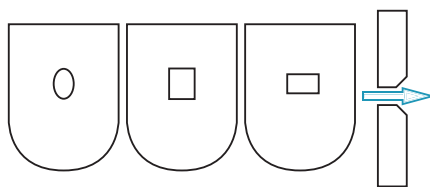


**FIG. 8.** Hole diameter and height of liquid above hole.

is rectangular, square or circular, or any random cut (TABLE 1). It is important to highlight that the issue with different shapes would be the friction factor and discharge coefficient of liquid. The discharge coefficient (Cd) of liquid through any hole is the ratio of actual flow to ideal flow. The Cd is inversely proportional to the friction factor; therefore, friction losses should be the lowest and the discharge coefficient should be the highest.

FIG. 7 shows a simple comparison on practical values. The discharge coefficient depends on the diameter (d) of the hole (circular shape) and the head (H) of the liquid in the product compartment. As the diameter of the hole or cut in the baffle increases, velocity reduces and fewer friction losses lead to a higher discharge coefficient. This should be optimized.

The head of the liquid in the product compartment also changes the friction losses. A higher head enhances the velocity and increases friction losses. Therefore, the minimum head should be there. The cut in the baffle should be smooth,



**FIGS. 9 AND 10.** A front view of a baffle with different hole shapes and a side view of the baffle, respectively.

even and fine to reduce friction losses.

**Size of the hole in the baffle.** The diameter of the hole should be determined based on the liquid load in the product compartment. In Part 1, it was seen in the calculation of the liquid that 20 tph (tons/hr) were accumulated there. As a result, the size or diameter of the hole is determined by the amount of liquid that accumulates per hour. Recommendation: The liquid velocity through the hole should be approximately 1.4 m/sec, and the height of the liquid in the product compartment above the hole should be 4 in., or 100 mm (FIG. 8).

For 20 tph (28.57 M<sup>3</sup>/hr with a density of 700 kg/m<sup>3</sup>) of flow toward the reboiler compartment, the hole size should be 42.5 mm, or approximately 2 in. Based on this recommendation (Eq. 2):

$$Q (\text{flow in m}^3/\text{hr}) = A \times V (\text{m/sec}) \times 3,600 \quad (2)$$

where A is the area of the hole and the velocity (V) is 1.4 m/sec.

Similarly, the hole diameter in the baffle can be calculated based on the liquid accumulation rate. A large-diameter hole in the baffle would equalize both levels of the compartments and the chances of bidirectional flow through this hole. This baffle reboiler has the preference of taking liquid from the reboiler compartment as well as the product compartment.

The liquid should not go from the reboiler compartment to the product compartment. If the efficiencies of once-through, circulating and preferential baffle reboilers are compared, the preferential baffle reboiler earns the second rank while providing operational flexibility.

FIG. 8 shows an ideal design of the baffle with a hole. The liquid head in the product compartment is 4 in. above the hole to make it unidirectional towards the reboiler sump, and the hole in the baffle is circular with a 2-in. diameter based on the

liquid accumulation rate. This does not affect the thermosiphoning of the reboiler.

FIGS. 9 and 10 show a front view of a baffle with different hole shapes and a side view of the baffle, respectively. The circular hole in the baffle is beveled towards the reboiler. This reduces the formation of eddies and friction losses of flowing liquid. All level transmitters should be in the product compartment. It might be assumed that with a hole in the baffle, level transmitters will work on any side; however, there is always a delta (difference) in the height of liquid on both sides. A high-high level alarm for the product compartment is helpful to avoid the submerging of the reboiler return line into the liquid pool.

**Takeaway.** The proper design of a preferential baffle reboiler can avoid startup and liquid accumulation problems and provide optimum benefits. Recommendations to enhance the design of the preferential baffle reboiler include:

1. The hole in the baffle should be circular rather than a rectangular or square.
2. The diameter of the hole should be calculated based on a velocity of 1.4 m/sec.
3. To avoid thermosiphon flaws, the elevation or altitude of the hole must be determined using a reboiler head calculation.
4. The hole or cut in the baffle should be smooth and beveled towards the reboiler compartment.
5. The baffle with an underflow design should be selected rather than the circulating reboiler; otherwise, a once-through reboiler is preferred. **HP**

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#### LITERATURE CITED

Complete literature cited available online at [www.HydrocarbonProcessing.com](http://www.HydrocarbonProcessing.com).

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## Bringing treatments to a boil

The function of a boiler is simple. It boils water to produce steam, which, in turn, provides energy. While this is a straightforward process, there are complexities within it that could affect the boiler's integrity. The primary concern is the quality of the water.

Even high-quality water contains impurities, which has the potential to create problems for the boiler's functionality. Over time, chemical impurities in the water could damage a boiler's internals, leaving solid deposits, such as corrosion, rust or scale as the steam evaporates. These accumulated deposits could eventually thermally insulate the boiler's heat exchanger surfaces, reducing the boiler's rate of steam generation and eventually causing the equipment's metals to fail. Without proper treatment, corrosion, rust and scale may eventually lead to thermal failure, reduced boiler efficiency and a potential boiler failure.

The boiler is not the only thing that may be affected by untreated feedwater. Aside from the boiler's internals, the corresponding safety equipment and auxiliary piping may also suffer the effects of water chemicals and impurities. Addressing the quality of the feedwater becomes imperative. Otherwise, the damage to the boiler and associated equipment may shorten their longevity and increase capital expenditures.

That is why a boiler water treatment plan is highly recommended to keep a boiler operating at a high and efficient level. Boiler water treatments neutralize or remove impurities and chemicals in feedwater to help ensure proper and effective functionality, and boiler longevity.

**Common challenges.** Common water contaminants are magnesium, calcium, iron, aluminum and silica, all of which can be found in hard water and result in hard

deposits when heated. Heated hard water serves as the primary source of scale in boilers. Scale buildup can reduce water flow in pipes and can prevent the efficient transfer of heat in boilers.

Corrosion stems from dissolved oxygen and carbon dioxide (CO<sub>2</sub>) in water. These gases attach to the walls of the boiler, piping and other equipment. Eventually, these gases may eat away at the metals within the equipment, causing corrosion, weakening the system. The weakened pieces are susceptible to cracks and other damage that can severely impact the boiler.

**Without chemicals.** Tackling these common challenges is best done through boiler water treatment, of which there are several options. One option does not require the use of chemicals. The two approaches under this method are using filters and softeners to remove chemicals and preheating

the water ahead of its entry into the boiler.

Sediment filters are designed to remove suspended solids in water, while water softeners remove magnesium, calcium and other impurities that cause hard water, which can result in scale buildup.

The second approach is preheating the feedwater before it enters the boiler. This process helps remove dissolved oxygen from the water, making it less harsh on the internals of the boilers and associated equipment. Preheating the water usually occurs in a feedwater tank or a deaerator using supplementary steam.

**The chemical approach.** Using chemicals to treat feedwater is an effective method for handling impurities, yet the amounts must be dispensed properly and accurately (FIG. 1). Too much of a chemical treatment may adversely impact the quality of the water, which could damage



**FIG. 1.** Using chemicals to treat feedwater is only an effective method for handling impurities if the amounts of chemicals are dispensed properly and accurately. This task can be achieved by employing the proper metering pump or filter feeder.



the boiler. Operators must be able to identify the right chemicals and then dispense them carefully.

Chemicals have a variety of functions when it comes to boiler water treatment.

Some are designed to maintain desired pH levels to minimize the water solubility, while others are used to absorb oxygen so it cannot cause corrosion.

There are four common chemicals

used to treat feedwater used in boilers: coagulants, phosphates, oxygen scavengers and chelants.

Coagulants are chemicals that make suspended particles in the feedwater flocculate or clump together. The clumped impurities, which take the form of sludge, pass through the water and sink to the bottom of the boiler. Operators typically use a boiler blowdown procedure to remove the sludge. Ferric chloride or hydrated potassium aluminum sulfate (alum) are the coagulants used in boiler water treatment.

The downside of coagulants is that the sludge that accumulates at the bottom of the boiler is corrosive and can still damage the boiler. Phosphates, such as sodium phosphate, are a way to combat this. Phosphates control the pH level in the water, as well as in the sludge, keeping corrosion at bay.

Another corrosion culprit is oxygen, which is why oxygen scavengers are a chemical option used to remove it from water. Oxygen scavengers include hydrazine and sodium sulfite. Lastly, chelants, such as nitrilotriacetic acid and ethylenediaminetetraacetic acid, are used to form ions with magnesium and calcium in the water to prevent scale buildup. Chelants are specialized molecules that can bind to positively charged metal ions and prevent them from forming insoluble precipitates.



**FIG. 2.** Because chemical injections are delicate processes that require precision, metering pumps serve as a viable option for effective boiler water treatment.

**Metering pumps for proper treatment.** Because chemical injections are delicate processes that require precision, metering pumps serve as a viable option for effective boiler water treatment (**FIG. 2**). The two pumping technologies that work best are hydraulically actuated diaphragm metering pumps and solenoid-actuated diaphragm metering pumps.

Hydraulic metering pumps work for chemical handling because they have a repeatable accuracy of  $\pm 1\%$ , which makes them ideal for injecting precise and controlled amounts of a chemical. Operators can constantly and consistently dispense the proper chemical amounts without concern. The pump's diaphragm is also hydraulically balanced, allowing it to operate against higher discharge pressures than a mechanically actuated diaphragm pump.

Additional features for this pumping technology include its robust nature and lifespan, which is designed to last 20 yr. These pumps also have an internal relief valve, the ability to inject chemicals at high



**FIG. 3.** Operating as a single piece of equipment that can inject water treatment chemicals while also acting as a filtration device, filter feeders continue to gain consideration for boiler water treatment because of this dual functionality.



pressures up to and beyond 4,000 psi (276 bar), automatic control with an electronic stroke control or variable-speed motor, and manual control through an adjustable micrometer dial.

Hydraulic metering pumps vary by model, with some having variable oil-bypass adjustment to provide improved valve performance. This oil-bypass adjustment enhances performance by allowing the pump's valve extra time to seat. These pumps can be constructed from several different materials, such as 316 stainless steel, C-20, polyvinyl chloride (PVC) and Kynar, all of which can handle a variety of chemicals. To meet certain service requirements, hydraulic metering pumps can also handle being outfitted with several motor configurations.

Solenoid-actuated or electronic metering pumps work well as an economical option for boiler water treatment. They provide chemical injection for low-capacity and low-pressure [less than 2 gph and under 250 psi (17.2 bar)] applications. These pumps have a repeatable accuracy of  $\pm 3\%$ , with some having stroke rates

of 300 strokes/min or higher, allowing for improved chemical injection at low flowrates. Many of these pumps can also operate at any single-phase voltage from 94 VAC–264 VAC and are unaffected by voltage fluctuations.

The pump's composition tends to be 316 stainless steel, PVC or Kynar pump heads; Viton or polytetrafluoroethylene (PTFE) seals; PTFE diaphragms; and 316 stainless steel and ceramic or PTFE check valves. These materials give these pumps versatility for several chemical injection applications during boiler water treatment.

Solenoid-actuated pumps also have several models with a manual frequency adjustment or speed control for stroking speed. Some models even have frequency adjustment and stroke-length adjustment, allowing for large turndown capabilities.

**The case for filter feeders.** Filter feeders are an option that continues to gain consideration for boiler water treatment because of their dual functionality (FIG. 3). They operate as a single piece of equipment that can inject water treatment

chemicals, while also acting as a filtration device by capturing the coagulated solids and impurities that cause rust, corrosion and scale.

Filter feeders use a filtration bag that captures nearly all contaminants, even those that are as small as 1 micron, which is five times smaller than the width of a human hair. These bags can also be disposed of after they are full, instead of being cleaned and used again, which can reintroduce captured particles back into the system.

**Takeaway.** While there are multiple ways to help ensure the integrity of feedwater for boilers, the most reliable method involves chemical treatments using metering pumps or filter feeders. These options provide tangible results that help maintain the boiler's optimal functionality and health throughout its lifespan. **HP**

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